SKI Perspective

Background

The start of site investigations with the purpose of identifying a suitable location for a spent fuel repository is an important step in the Swedish programme for radioactive waste. The Swedish Nuclear Waste Management Company (SKB) has as a basis for these investigations specified requirements on the rock that must be fulfilled (SKB TR-00-12) and a general programme describing the objectives and methods (SKB R-01-10). The Swedish government has requested that SKB should initiate a consultation with the Swedish Nuclear Power Inspectorate (SKI) as well as the Swedish Radiation Protection Authority (SSI) covering the initial and complete phases in the site investigation programme.

This report will be used by SKI as a basis for assessing SKB's initial geochemical characterisation efforts as well as the specified geochemical requirements of the selected sites. A comprehensive understanding of chemical conditions of the groundwater system is needed in order to ensure that the stability of engineered barriers are favourable and that the credit taken for radionuclide retardation is consistent with site specific conditions.

The importance of an initial assessment of SKB's geochemistry programme is related to the fact that site investigation activities may disturb the initially unaffected conditions. The best opportunity of receiving an accurate picture of e.g. the distribution of various groundwater types is therefore at the start of the site investigations. The value as evidence of geochemical information for the subsequent stages of interpreting data and assessing the long-term safety at a particular site will be enhanced if potentially controversial issues have been thoroughly described, debated and if possible resolved, at an early stage.

Relevance for SKI

This report provides a starting point for SKI's assessment of the selection, measurement and interpretation of various geochemistry parameters within the SKB site characterisation programme.

Results

The objectives of this project have been fulfilled. They included a review of the relevance of geochemical parameters for the assessment of long-term safety, an assessment of SKB's sampling and measurement methods as well as an overview of potential disturbances.

Future work

Future work may include an extended interpretation and assessment of the stability of the geochemical conditions during a glaciation cycle. It is also possible to in greater detail address the usefulness of isotope geochemistry characterisation as well as mineralogical and chemical analysis of solid samples.

Project Information

SKI project manager: Bo Strömberg
Project Identification Number: 01097

Abstract

SKB has described its approach to site characterisation in a number of Technical Reports (Andersson et al. 1998, 2000; SKB 2000a,b). One of the scientific topics in which specific information requirements and priorities are set out is geochemistry. This report for SKI examines critically whether the geochemical parameters identified in the SKB programme documents will be adequate for safety and regulatory requirements. It also examines some of the details of parameter requirements and interpretation tools that will be necessary to convert site investigation data into knowledge about chemical conditions and groundwater movements.

The SKB strategy for geochemical data focuses on a small number of 'suitability indicators', primarily dissolved oxygen, pH and salinity. Their parameter requirements aim to assess those primary characteristics, as well as to acquire a wider range of data that will support those assessments and provide a broader understanding of candidate areas. An initial observation in this review that, though it is a primary suitability indicator, dissolved oxygen apparently will not be measured and instead will be inferred from other redox indicators. This raises a number of issues about sampling and monitoring measures, analytical data reliability and sensitivity, and the degree of confidence in geochemical understanding.

A geochemical programme involves reconnaissance by desk study and acquisition of new data at levels of details that are appropriate to the stage of site investigations. As early as possible, a conceptual model of a candidate area should help to define the objectives of geochemical measurements on both rock and groundwater samples.

It is recommended that parameters requirements should be defined and considered not only in terms of isolated measurements but more in terms of addressing broader objectives that relate to safety and also to geoscientific understanding. The safety priorities remain (e.g. dissolved oxygen) but will then be supported by an understanding of processes. This approach will also help to clarify the rationale for taking samples and making particular measurements and will indicate the tolerances in terms of data error and interpretative uncertainty.

Geochemical parameters that are required from rock, mineral, water and dissolved gas samples are listed and discussed along with the reasons for requiring the data. Measures that need to be taken to optimise the quality and representativeness of samples are also discussed because these are paramount in determining the ultimate reliability of data.

Finally, interpretative tools that are used to convert raw data into knowledge and confidence in understanding of processes have been briefly considered. These may have additional 'supporting' data requirements and also need to be critically reviewed for their applicability and for the robustness of the conceptual models on which they are based.

Sammanfattning

SKB har beskrivit sitt tillvägagångssätt för det planerade platsundersökningsprogrammet i ett antal tekniska rapporter (Andersson m.fl. 1998, 2000; SKB 200a,b). Geokemi är ett av de tekniska områden där uppsättningen av erforderliga informationsbehov och prioriteter anges. Denna rapport överväger huruvida de geokemiska parametrar som SKB identifierat är tillräckliga för myndigheternas krav och utvärderingen av långsiktig säkerhet. Rapporten undersöker också vissa detaljerade krav med avseende på specifika parametrar och tolkningsverktyg som är nödvändiga för att överföra data från platsundersökningar till kunskap om geokemiska betingelser i djupa grundvatten och grundvattenrörelser.

SKB:s strategi för geokemisk karakterisering och urval av parametrar fokuserar på ett litet antal lämplighetsindikatorer, primärt löst syre, pH och salthalt. SKB:s urval av parametrar syftar till att utvärdera dessa primära lämplighetsindikatorer, liksom även att förvärva ett bredare urval av data som understödjer denna utvärdering och att skaffa en generell förståelse för kandidatplatserna. En tidig observation under denna granskning är att även om syre är en primär lämplighetsindikator kommer den inte att mätas utan istället härledas från andra redox-indikatorer. Detta ger upphov till en rad frågeställningar om provtagning, tillförlitlighet och känslighet för analytiska metoder samt graden av vetenskaplig förståelse för geokemi.

Ett geokemiskt mätprogram involverar förberedande litteraturstudier och ackvisition av nya data med en detaljeringsgrad som avpassats efter hur långt fortskriden platsundersökningarna anses vara. En konceptuell modell över kandidatområdet bör upprättas så snart som möjligt, vilken skall underlätta definitionen av målsättning av geokemiska mätningar av både berg- och grundvattenprover.

Krav på parametrar bör definieras och övervägas inte bara i termer av enskilda mätningar utan hellre i termer av mera omfattande målsättningar som relaterar till långsiktig säkerhet liksom geovetenskaplig förståelse. Prioritering med utgångspunkt från långsiktig säkerhet kvarstår (t.ex. löst syre) men kan då understödjas av en förståelse av processer. Detta tillvägagångssätt skulle också klargöra den logiska bakgrunden för provtagning, särskilda mätningar samt toleranser för mätfel och tolkningsosäkerhet.

I denna rapport diskuteras geokemiska parametrar som erfordras från berg- och mineralprover, grundvatten och lösta gaser, liksom även anledningarna för att mäta just dessa parametrar. Åtgärder som krävs för att optimera kvaliteten och representativiteten av prover diskuteras också eftersom dessa är av överordnad betydelse i utvärderingen av hur pålitliga erhållna data kan anses vara.

Slutligen övervägs vissa tolkningsverktyg som används för att överföra primärdata till kunskap och tillförsikt i förståelsen av processer som har översiktligt diskuterats. Användning av dessa tolkningsverktyg kan medföra ytterligare krav på underbyggande data och behöver granskas kritiskt med avseende på deras tillämplighet och med avseende på hur robusta underliggande konceptuella modeller kan anses vara.

Contents

List of Tables

List of Figures

1.   Introduction

1.1   Background

This report is the result of a contract (Ref. 14.9-010482/01097; April 2001) from SKI (Project Manager: Dr Bo Strömberg) for a Review of Geochemical Parameters Required from the SKB Site Characterisation Programme.

The work is motivated by the imminent start of the SKB investigations in the municipalities of Tierp, Oskarhamn and Östhammar. Initial site investigations in these areas will lead to the identification, if such exist, of suitable sites for more detailed investigations.

Technical background to the selection of candidate areas and to the parameter requirements in all geoscientific aspects is contained in a number of SKB reports and also in the outcome of the safety assessment exercise SR97 which was a dry-run for the KBS-3 repository concept in three 'typical' sites.

The background to SKI's regulatory approach, and specifically to geosphere parameter requirements, is contained in the SITE-94 performance assessment (Geier et al. 1996), for which geochemical characterisation was tackled in detail by Glynn and Voss (1999). A recent response from SKI to the outline proposals by SKB for its site investigation and selection methodology is contained in SKI (2001).

Some of the interim conclusions of this review were discussed at a Site Characterisation seminar convened by SKI and SSI at Johannesberg Slott, near Stockholm, on 9 November 2001. That seminar signalled the initiation of the INSITE group that will advise SKI in overseeing the site characterisation activities of SKB, taking forward the parameter requirements and interpretative methods that SKI has to consider.

It is important to realise that the geochemical issues discussed here are one of many aspects of repository safety, siting and design of which the regulators will take account. What is discussed here as a 'priority' in terms of geochemical parameters has also to be evaluated in the context of the overall safety assessment and the general credibility of site selection. Those issues are beyond the scope of this review, which is limited to geochemistry.

1.2   Objectives and Rationale

The purpose of this review is to examine critically the strategy that SKB has set out for obtaining geochemical information and knowledge for use by themselves in making future safety assessments and by SKI for future regulatory analyses.   A question that SKI has to address is whether these parameters will be representative, reliable and generally appropriate for the safety and regulatory requirements.   In addition there is an issue of whether the acquired parameters and interpretations will earn the confidence of external review groups and the wider public. Site evaluation and acceptance needs to be underpinned by demonstrable understanding of 'how the host geosphere rock-water system works', in a wider context than just the narrow prescription for safety assessment.

A critical examination is timely because SKB has described its approach in detail in a number of Technical Reports (Andersson et al. 1998; SKB 2000a; SKB 2000b) and is at an advanced stage of planning site investigation tactics to acquire the required parameters for three candidate municipality areas. These will be characterised for site selection and potential acceptance on the bases of open comparison of attributes, of predicted safety, and of how well the rock systems are understood in a scientific sense. Not only will safe future performance be dependent on certain geochemical properties, amongst many other parameters and interpreted properties, but elimination of potential sites may also be dependent on geochemical parameters and interpretation.   Two requirements and criteria for data acquisition have to be addressed. Firstly, data need to be prioritised so that parameters that are of direct and quantitative significance for safety will be measured to agreed standards of reliability. Secondly, there needs to be an understanding of the context, significance and potential uncertainties of other parameters and interpretative models that may increase understanding of chemical and hydraulic processes but also may have higher levels of uncertainty.   Examples of the latter category include measurements and interpretations using 'state of the art' methods that are topics of ongoing research, and interpretations for which there are alternative models that increase overall uncertainty.

This review makes some suggestions for the approach that SKI takes in terms of requirements for geochemical information from the SKB sites programme.

Geochemistry is a difficult area of site investigation, for a number of scientific and practical reasons. There are a multitude of different measurements that can be made, with varying degrees of complexity and difficulty, on both rock and water media. Values for many of these parameters are prone to perturbations from the measurement method itself and from other site investigation activities, so that confidence about the 'in situ' conditions can become an issue. Geochemical measurements mostly require some sort of model interpretations to provide information that is relevant to the site investigation objectives, and often the methods and uncertainties in these interpretations are not evident to non-specialists. Therefore the approach proposed here gives priority amongst geochemical investigations to making measurements and achieving adequate understanding of the principal suitability and safety criteria. For

difficult parameters, fewer measurements with higher reliability are preferable to masses of uncertain data with open-ended significance.

Building on the present achievements in understanding the spatial variability and principles of groundwater geochemistry in crystalline rocks, the proposed principles for data collection are:
o   Use desk study at the outset to estimate parameters, to set-up hypotheses for what will be found, and to prognose difficulties in meeting requirements;
o   Limit the extent of the primary data requirements to achieve simplicity and transparency, and to reduce the scope for contention;
o   Design data acquisition to achieve specific levels of knowledge of the system;
o   Agree targets and criteria for data reliability that are realistic and achievable;
o   Understand the qualifications on data that may limit how they can be used by non-experts;
o   Tie in 'first level' interpretation directly with data collection so that the significance of data is evident at the time of measurement.

2.   SKB Site Characterisation Plans

The SKB position on the categories and uses of geochemical parameters has been stated in a number of recent reports contributing to the development of the present site characterisation strategy. The 'Parameters Report' (Andersson et al., 1998) discusses data requirements in categories defined by the conventional branches of geoscience (hydrogeology, chemistry, etc). A detailed rationale for hydrogeological information and its uses is given. Geochemical information is described in terms of a chemical model of groundwater and of its interactions with minerals and repository materials. This model provides the chemical parameters that are of primary importance to safety assessment, specifically to canister corrosion, bentonite performance, fuel dissolution and solubilities, and radionuclide retention in the far field. These chemical parameters are listed in Tables 6-2 to 6-5 of the 'Parameters Report', and are summarised here in Table 2.1.

In addition to the 'performance' parameters, the 'Parameters Report' also identifies a range of hydrochemical and environmental isotopic data that will contribute to geoscientific understanding of the system evolution, of solute transport, of water flow direction and ages, and of natural trace element geochemistry as a guide to radionuclide behaviour. The parameters list for this purpose is in Table 6-6 of the 'Parameters Report'.

Table 2.1. Groundwater chemistry parameters of importance for repository performance (distilled from Andersson et al. 1998)

	Canister corrosion		Bentonite performance		Spent fuel dissolution		Radionuclide retention	
	Essential	Limited	Essential	Limited	Essential	Limited	Essential	Limited
TDS			✓					
pH		✓		✓		✓	✓	
Eh	✓				✓		✓	
Na^+			✓				✓	
Ca^{2+}			✓				✓	
K^+			✓					
Mg^{2+}			✓					
Cl^-	✓						✓	
SO_4^{2-}		✓						✓
HCO_3^-		✓				✓	✓	
Fe^{2+}	✓				✓		✓	✓
HS^-	✓				✓		✓	✓
SiO_2				✓				
Al^{3+}				✓				
N species	✓							
DOC		✓						
HA & FA							✓	
HPO_4^{2-}		✓						✓
F^-								✓
Mn^{2+}								✓
N_2/CO_2							✓	
H_2		✓					✓	
CH_4		✓					✓	
He/Ar							✓	
colloids							✓	
bacteria		✓					✓	

The rationale for data requirements in the 'Parameters Report' also lies behind the SKB position on what properties of the rock and groundwater system can be used for siting and evaluation of sites. Essentially, the report on 'what is required from the rock' presents a set of suitability indicators and criteria (Andersson et al., 2000). It thus effectively prioritises the data requirements covered in the 'Parameters Report'. It also distinguishes between criteria that can be applied at the feasibility study, site investigation, and detailed characterisation stages of site selection and evaluation, depending on the extent of available knowledge at each stage. Requirements and preferences are identified, the former being prohibitive criteria and the latter providing guidance to what are likely to be suitable conditions as indicated by a safety assessment. The hydrochemical suitability indicators are listed in Table 2.2. A geochemical context, or 'function analysis' is also identified – this is essentially a rationale or model for the particular indicator parameter and in some cases identifies sets of additional parameters that support a 'more precise definition' of the indicator. Two observations are made: firstly, that dissolved oxygen (DO) concentrations *per se* are absent from lists in both reports, and, secondly, that the absolute requirements are somewhat modified. For example, the 'Requirements Report' asserts that if none of the Eh indicators can clearly demonstrate the absence of dissolved oxygen, a deeper

chemical assessment is required. In other words there remains some doubt about measuring this key requirement reliably. This issue is discussed further in Section 3.2.5.

Table 2.2. Suitability indicators for groundwater compositions, to be applied at the site investigation stage (from Andersson et al. 2000)

Parameter	Requirement (Req) or Preference (Pref)	Criteria in Site Investigation
Dissolved O_2	Req: Absence at repository level (indicated by negative Eh, occurrence of Fe^{2+} and/or HS^-)	At least one of Eh, Fe^{2+} or HS^- must be satisfied
pH	Pref: Undisturbed groundwater at repository level should have pH between 6-10	Values should be in range 6-10 below –100m depth
TDS	Req: TDS <100 g/l	Values at repository level must be <100 g/l. Occasional higher values OK if located in areas that can be avoided
Others	Pref: DOC <20 mg/l Pref: Colloids <0.5 mg/l Pref: Low NH_4 Pref: $Ca^{2+}+Mg^{2+}$ >4 mg/l at rep. depth Pref: Low Rn and Ra	Attention to deviations from preferred concentrations

3. Acquisition of Geochemical Data

3.1 Reconnaissance by Desk Study

Existing data from shallow wells and from SKB's previous research investigations have been looked at in the feasibility studies of six municipalities (SKB, 2001a). For the three municipalities at which initial site investigations are planned to start in 2002, previous deep borehole studies by SKB supplement the information on groundwater compositions that is available from shallow water wells. Previous studies at Finnsjön are relevant to Östhammar and Tierp, and the Äspö/Laxemar studies are relevant to Oskarshamn. Desk study should therefore maximise the value of existing data and get some insights of likely parameter ranges in new site investigation and also of potential sample quality difficulties.

Water samples from the Finnsjön investigations were thought to have been generally of relatively poor quality (versus Äspö and Gideå samples) by Laaksoharju et al., (1998), based on the quality scoring method for assessing representativeness (Laaksoharju et al., 1993). However reasonable confidence was expressed in a reference water selected to be typical for water at repository depth at Finnsjön (Table

3-1 in Laaksoharju et al., 1998). A second potential reference water from similar depth at Finnsjön was considered to be a poorer sample. Its salinity was about 10% of that of the other reference water. No data for dissolved oxygen (DO), or for Fe^{II} or Fe_{tot} were reported for that sample, and HS^- was below detection limit of 0.01 mg/l. Dissolved uranium, U, was reported as 19.3 μg/l and was suspected to be relatively high due to oxidation during drilling. This reference water is Ca-Na/Cl composition, with 5500 mg/l Cl and 9457 mg/l TDS. pH is reported as 7.04, but the saturation index of calcite is –0.20, suggesting that the pH may be 0.20 too low. Carbon-14 is reported as 34.4 pmC (percent modern C), which translates to a model ^{14}C-age for the water of <10,000 years. Thus groundwater flow times from recharge to repository depth might be amenable to estimation by isotopic measurements although the possible effect of contamination of this water sample has to be considered.

Table 3.1 Indicative analyses of SKB reference waters (first three columns) and two other representative groundwaters (last two columns) from regions adjacent to SKB's proposed site investigations

	Finnsjön[1] (adjacent to Östhammar and Tierp)		Äspö[2] and Laxemar[3] (adjacent to Oskarshamn)		
Depth m	439	511	530 ([2])	798-804 ([3])	1631-1681([3])
Na mg/l	1700	275	2100	288	8500
K mg/l	13.0	2.0	8.1	4.5	45.5
Ca mg/l	1650	142	1890	123	19300
Mg mg/l	110	17	42	10.6	2.12
Cl mg/l	5500	555	6410	548	47200
SO$_4$ mg/l	370	49	560	105	906
HCO$_3$ mg/l	47	278	10	111	14.1
DOC mg/l	-	5.7	1.0	5.0	0.9
Fe^{II} mg/l	-	1.80	0.24	1.71	0.43
HS$^-$ mg/l	<0.01	-	0.15	<0.01	<0.01
U μg/l	19.3	0.35	3.86	0.87	0.013
pH	7.04	7.90	7.73	7.6	7.3
Eh	-	-250	-308	**-120 (-317)**	-300 (-334)
^{14}C pmC	34.4	-	-	-	-
TDS	9457	1339	11107		

[1] from Laaksoharju et al., 1998; [2] from Laaksoharju et al.,1998; [3] from Laaksoharju et al., 1995a and 1999a.

There are, of course, a large number of data for shallow and deep boreholes and from samples taken in the underground laboratory at Äspö which are relevant to a desk study of the Oskarshamn area. The reference water for typical repository depth is a Ca-Na-Cl water with 11,107 mg/l TDS (Laaksoharju et al., 1998). Data indicative of redox conditions include 0.15 mg/l HS$^-$, 0.24 mg/l Fe^{II} and 3.86 μg/l U. No ^{14}C data are reported, therefore there are no indications of flow times. Two other sets of groundwater analyses, both from the deep borehole at Laxemar (1705 m total depth), are given in Table 3.1. The first of the Laxemar samples, from just below repository depth, illustrates the decreasing salinity of groundwater relative to the Äspö at similar depth. The second of these is well below repository depth, but it exemplifies the

increasing salinity of water in this region of rock. The Eh values shown in brackets for these two waters are those that were calculated on the basis of Fe^{II} redox control according to the Grenthe et al. (1992) model.

With the background knowledge provided by these reference waters and the general data sets for Finnsjön and Äspö, it should be possible to construct preliminary conceptual models for groundwater geochemistry for each of the initial site investigation areas. The conceptual models should take into account preliminary ideas about groundwater flow directions, including recharge and discharge zones, based on topography of the water table. The conceptual model would lead to predictions or hypotheses of geochemical variation within each area. Initial site investigations, specifically the locations of 'hydrochemical' boreholes, should be planned in the context of investigating the hypotheses.

The approach taken in a reconnaissance by desk study should be along the lines of:

1.   Review quality scores of water samples to rank reliability of samples

2.   Assess reliability of individual determinands of interest,
       e.g. TDS, Cl, Fe^{II} or Fe^{tot}, DO, HS^-, SO_4, DOC, pH, Eh, U, $\delta^{18}O$, δ^2H, ^3H, ^{14}C.

3.   Exclude data where reliability is insufficient relative to the acceptable tolerance for that determinand.

4.   Use accepted data to obtain an initial view of spatial variability of geochemical variables.

5.   Evaluate data that are anomalous – decide whether they are artefacts or apparently representative, or leave as open queries to be followed up in subsequent investigations.

6.   Construct a preliminary conceptual model for groundwater geochemistry taking into account these hydrochemical data, groundwater flow ideas, and also theoretical/generic considerations about hydrochemistry (e.g. groundwater compositions in Fennoscandian bedrock, possible influence of Baltic water if close to coast, etc).

Another group of geochemical parameters that should be reviewed in a desk study is bedrock compositions, i.e. the 'typical' chemical compositions. A data set for typical composition of each rock category expected at a site would include major elements, significant minor/trace elements, petrographic and mineralogical information. This information would allow early prediction of some geochemical properties as well as providing a context against which specific data from the investigated site would be compared. Required geochemical properties include:

o   Overall comparison with average compositions and identification of geochemical anomalies;

o   Assessment of resource potential, e.g. potential base metal and valuable trace element contents;

o   Rock geochemistry (i.e. U, Th, Li, B, etc) controlling the production and release to groundwater of radiogenic helium, and the 'in situ' production of natural radionuclides (e.g. ^{3}H, ^{36}Cl);

o   Fluid inclusion distribution and compositions i.e. salinities, trapping temperatures;

o   Abundances and proportions of trace constituents in rock that might influence interpretation of groundwater chemistry, e.g. Cl, Br in biotite;

o   Stable oxygen and hydrogen isotope compositions of whole rock and separate mineral phases, as indicators of extent of matrix alteration by water-rock reaction.

3.2   Initial Site investigations

Initial site investigations will have the aims of (SKB, 2000a):

o   Identifying and selecting the site within a candidate area that is deemed to be most suitable for a deep repository and thereby also the part to which further investigations will be concentrated;

o   Determining, with limited efforts, whether the feasibility study's judgement of the suitability of the candidate area holds up in the light of in-depth data.

To allow comparisons between areas, they should be brought up to a comparable knowledge level by the initial site investigations (SKB, 2000a). Comparisons between areas and selection of favourable site within areas will require knowledge at both the scales of the candidate areas and of a typical site for complete investigation. The level of knowledge should be adequate for:

o   Preliminary understanding of areas and sites;

o   Preliminary design of repository;

o   Preliminary judgements of safety.

The geochemical parameters that are required to improve understanding and to feed in to judgements of safety fall into a number of groups. The groups of parameters indicate different sample types and different analyses and analytical methods (Table 3.2). Some details of the specific parameters that should be expected in each category are given in the following paragraphs. The uses of data are also discussed. Sampling and analytical issues are discussed in Chapter 5.

Table 3.2   Groups of geochemical parameters for rock and water media that are required from the initial site investigations.

Medium	Sample types	Analyses and other information
Rock	Drillcores, outcrop samples	Bulk rock composition, major and trace elements
	Drillcores – thin sections	Petrography of rock fabric, alteration, microporosity
	Drillcores – thin & polished sections, stubs	Identity and composition of matrix minerals including trace minerals
	Drillcores – stub mounts & polished sections	Identity and composition of fracture-filling minerals including clays
Water	Groundwater in shallow boreholes	Chemical and isotopic composition including on-site measurements of unstable parameters
	Groundwater in deep boreholes (discrete intervals)	Chemical and isotopic composition including on-site measurements of unstable parameters
	Surface water (lakes, streams and springs)	Chemical and stable and isotopic composition
	Baltic seawater (if coastal site)	Chemical and stable isotopic composition
	Rainwater	Chemical and stable isotopic composition
	Groundwaters in gas-tight containers	Dissolved gases (quantity and chemical composition)

3.2.1 Bulk Rock Compositions

Chemical compositions of bulk rock should be measured for a suite of samples that is representative of the range of rock types in the candidate area. In addition to the basic geochemical characteristics of the rock, from which normative calculations of mineral content can be compared with petrographic observations, the concentrations of trace components have various uses. These are listed in Table 3.3. The use of U and Th data with various trace element abundances for calculating in situ production in the Stripa granite is described by Andrews et al. (1989).

Table 3.3 Chemical parameters in analyses of bulk rock samples, and the purposes for which data can be used

Element	Typical range	Use of Data
SiO_2		Normative composition
Al_2O_3		Normative composition
Na_2O		Normative composition
K_2O		Normative composition
CaO		Normative composition
MgO		Normative composition
FeO		Normative composition + reducing capacity
Fe_2O_3		Normative composition
MnO		Normative composition + reducing capacity
Ba		Normative composition
Sr		Normative composition + Sr isotope ratio
TiO_2		Normative composition
P_2O_5		Normative composition + complexing phosphate
Total SO_2		Normative composition + reducing capacity
Total CO_2		Normative composition
F		Complexing fluoride
Cl		Salinity origin
Br		Salinity origin
Li		Tritium production
B		In situ neutron absorber + B isotope ratio
Be		In situ neutron absorber
As		Excavation & disposal hazard
Ge		In situ neutron absorber
REEs (inc Y)		Comparison with REE patterns in water
Co, Cr		Ore mineral potential
Ni, Cu, Zn		Ore mineral potential
Ag, Au		Ore mineral potential
Pt, Pd		Ore mineral potential
Rb		Sr isotope ratio interpretation
V		Ore mineral potential +U complexation
U		Dissolved U source + in situ isotope production
Th		Dissolved Th source + in situ isotope production

3.2.2 Petrography and Mineralogy of Rock Matrix

Petrographic observations, estimates of mineral composition and identification of trace mineral phases are necessary for a number of purposes. Petrography by optical microscopy and SEM (scanning electron microscopy) will provide descriptions of:

o   Extent of alteration of primary minerals texture

o   Microporosity and micro-fracturing

o   Major minerals and estimates of composition

o   Abundance of fluid inclusions

o   Trace minerals that are significant for geochemical interpretation, e.g. monazite, uraninite, pyrite, barite, etc.

Alteration which leads to the enhancement of microporosity, especially around water-bearing fractures, is significant because the microporosity may become the dominant source/sink for solutes (Mazurek et al, 1997; Mazurek, 1998; Mazurek et al., 2000a). The description of microfracturing, alteration of matrix adjacent to conductive fractures, and of the effects of hydrothermal alteration on the reducing capacity due to FeO in wall-rock is also reported in Mazurek et al. (2000b), Eliasson (1993) and Tullborg (1995). Measurements of rock matrix porosity in crystalline rocks by various methods, and the comparability of data, are reported in Rasilainen et al. (1996). Matrix porosity is a distinguishing feature of crystalline rock lithologies (Mazurek et., 1997).

Trace minerals need to be positively identified because their presence or absence is often important for understanding how water-rock reaction controls the composition of groundwater, especially with respect to trace solute (Bruno et al., 2001). These may be significant analogues for radionuclide solubility and mobility. The major aluminosilicate minerals are more predictable on the basis of petrographic study. Some of the trace minerals and the trace elements in groundwater that may be controlled by them are:

-    monazite   -   U, Th, REEs
-    zircon   -   Zr, U
-    apatite   -   P, Th, REEs, Y
-    barite   -   Ba, Ra
-    fluorite   -   F, P
-    xenotime   -   P, Y, REEs
-    bastnaesite -   REEs, F

Matrix diffusion into intact rock may be a key mechanism in the transport model of the safety assessment, depending amongst other things on the potential rôle of fracture-filling material in retarding solute movement. However the extent into the intact rock that this operates is variable and rather controversial (e.g. Ohlsson and Neretnieks, 1995). Evidence that assists in forming a view on this matter, and perhaps is able to distinguish between rock types and sites in terms of matrix alteration and porosity, is required in the initial characterisation of sites.

3.2.3 Abundance and Mineralogy of Fault Rock and Fracture Fillings

Petrographic and mineralogical study of fault rock and fracture fillings is important in two ways: (i) They are the solid materials in groundwater flow paths that are the primary medium for retarding transport of radionuclides (Landström & Tullborg, 1995), and (ii) Some of these minerals are likely to be in geochemical equilibrium with groundwaters and are therefore good indicators of how chemical conditions, especially pH and redox, are regulated. In addition, there may be fracture minerals that are not reacting with present groundwater and that preserve a geochemical record of past groundwater conditions, i.e. of long-term stability or otherwise.

A prerequisite for getting reliable information about such materials is that they are sampled carefully. Cored drilling must be specified to preserve friable and soft fault/fracture-fill materials that wash out easily (see Table 4.1; Bath et al., 2000).

Geochemical and mineral analyses by a variety of methods that may include XRD (X-ray diffraction) and analytical SEM (scanning electron microscopy) will measure:

- o   Mineral phases (e.g. calcite, iron oxides, pyrite, clays, chlorite/biotite)

- o   Transport porosity in fracture

- o   Morphology and zoning of major infill minerals e.g. calcite

- o   Redox-sensitive indicators e.g. Fe^{II}/Fe^{III} in chlorite/biotite

- o   Cation exchange or sorption properties of gouge clays.

The potential significance of quantitative analyses of the amounts and compositions of fault/fracture infills is explained by Mazurek et al. (1997). The material that constitutes the flow-wetted surface is distinct from the bulk rock. Mineralogy and the arrangement of unfilled porosity in fractures/faults may also differ between rock types and could be a significant feature that distinguishes sites. However it has been noted that spatial variability of fracture infillings probably averages out over the scale of transport paths from repository to surface, thereby justifying reliance upon reasonable averaging of these parameters (Thury et al, 1994).

3.2.4 Chemical Compositions of Shallow Groundwaters

Shallow groundwaters are of interest in initial site investigations for a number of reasons:
- (i)   They are the interface between the geosphere and biosphere, containing groundwater pathways for radionuclide transport, dilution and transfers to potential receptors;
- (ii)   Recharge and discharge zones for the whole groundwater system can be identified by study of shallow groundwaters;

(iii)   Understanding flows and compositions of shallow groundwaters is a prerequisite for understanding deeper groundwaters.

Groundwater at shallow depths is not a direct input to the near field model for a deep repository, so the emphasis of these data is on ensuring that the flow and composition of the actively-flowing part of the groundwater system is understood.

The priority should be placed on obtaining reliable data describing the inputs to (or outputs from) deeper groundwater. Objectives that set parameter requirements for shallow groundwaters include:

o   Attenuation of dissolved oxygen with increasing depth and regulation of redox conditions;

o   Identification of groundwater recharge and discharge zones by variations in chemistry, e.g. salinity, dissolved helium, tritium;

o   Sources and sinks of acidity (H^+) and identification of reactive minerals that take part in water-rock reactions and equilibria;

o   Water sources and groundwater 'ages' i.e. transit times and solute residence times, environmental isotope systems;

o   Natural radionuclide abundances and mobility: U and Th series including Rn;

o   Dissolved organic material and colloidal materials that are mobile in groundwater;

o   Baseline conditions for parameters (especially those that will be disturbed by site investigation activities) that will be monitored in the future.

A list of specific geochemical parameters and their principal uses for these objectives is in Table 3.4. This list is quite similar to Table 6.6 in Andersson et al. (1998; the 'Parameters Report' from SKB), except that here the requirements are focused on understanding shallow groundwaters which have not been considered explicitly. A similar list can be constructed for groundwaters at repository depth (see Table 3.6).

The priorities should be objectives that have direct or indirect implications for safety assessment. These are the objectives concerned with redox controls, groundwater travel times and zones of groundwater discharge to the biosphere.

Table 3.4   Geochemical parameters required from investigations of shallow groundwaters

Parameters	Reasons for requiring data
pH	mineral equilibria, H^+ sources/sinks
Salinity, electrical conductivity	water and solute sources discharge zones, seawater intrusion (coastal sites)
DO, Eh	redox, attenuation of dissolved oxygen
Na, K, Ca, Mg	main chemical components
HCO_3, TIC	carbonate mineral equilibria, pH control
SO_4, HS	redox
Cl, Br	salinity, origins of salinity
NO_3, NH_4	recharge zone, redox
Fe^{2+}, Mn	redox
DOC	redox control, colloids
$^{18}O/^{16}O$, $^2H/^1H$	water sources
^{13}C, ^{14}C(TIC), ^{14}C(DOC)	carbon sources, water age, biological activity
^3H	recharge zone, recent infiltration
U, Th, Rn	natural radionuclides, redox (U only)
He	discharge zones, older groundwater
^{36}Cl	input to deeper Cl, solute residence times

Baseline parameters are another priority, for which the overall requirements are to describe the groundwater compositions in the natural state and to understand the fluxes of geochemical components that could be indicators of chemical or radiological leakages to the biosphere. Parameters that fall in this category include Rn, He, Cl, pH.

3.2.5 Chemical Compositions of Deep Groundwaters

Some quite specific requirements on the host rock and the groundwaters in the vicinity of a repository have been set by SKB (Andersson et al, 2000). These include some requirements and preferences for the chemical composition of groundwater that might affect the performance of the repository. The influence of groundwater composition has been described in terms of four key aspects of the multi-barrier concept for repository safety:

1.   Integrity of the spent fuel canister – corrosion of copper leading to failure of containment.

2.   Low solubility of spent fuel and slow dissolution – accelerated release of radionuclides to water within the canister.

3.   Stability and swelling of the compacted bentonite buffer and performance of bentonite in retaining radionuclides – loss of swelling pressure and dispersion of bentonite.

4.   Retardation of radionuclides in surrounding rocks – loss of retarding capability due to sorption, co-precipitation and matrix diffusion.

SKB specifies the chemical parameters that are required to address these aspects in the 'Parameters Report' (Andersson et al., 1998). These are summarised in Table 2.1.

The rationale for the priority analyses of deep groundwater samples is explained in Table 3.5. The objectives for many parameters are focussed directly on the impact of groundwater on the repository near field, in contrast to data for shallow groundwaters that are concerned with understanding the groundwater system.

Table 3.5   Geochemical parameters required from initial investigations of deep groundwaters

Parameters	Reason for requiring data
pH	canister corrosion, radionuclide solubilities, speciation
HCO_3	carbonate equilibria controlling pH, complexation
Salinity, TDS	bentonite stability, competitive sorption
DO	canister corrosion, redox conditions for fuel dissolution and speciation
Na, K, Ca, Mg	competitive sorption on bentonite, stability of compacted bentonite, loss of swelling capacity
Eh, Fe^{2+}, HS/SO_4	redox conditions for dissolved and speciation, proxy indicators for dissolved oxygen, sulphide corrosion of copper
DOC, colloids	redox conditions, colloid formation and complexation
NH_4	canister corrosion
Rn, U, (Ra)	radiological hazard of excavation, redox indicator (U only), analogue radionuclides
Cl, Br	total salinity, sources of salinity
Si, Al	geochemical model for bentonite stability (see text)
$^{18}O/^{16}O$, $^{2}H/^{1}H$	water sources
^{13}C, $^{14}C(TIC)$	carbon sources, biological activity, water age*
^{3}H	recent infiltration*
^{4}He	old groundwater*, flow heterogeneity and mixing

Notes: * Other isotopic and chemical methods for diagnosing young and old groundwaters, such as CFCs and SF_6 which are anthropogenic volatile compounds appearing as traces in young groundwaters, and ^{36}Cl as both thermonuclear and natural tracer, should be considered in addition to ^{3}H, ^{14}C and ^{4}He; these may require special sampling and analytical logistics.

The list of parameters in Table 3.5 is similar to parameters in Tables 6.2 to 6.6 of Andersson et al. (1998). The most significant difference is that Table 3.5 includes dissolved oxygen (DO) in addition to the 'proxy' measurements of Eh, Fe and HS. Some of the parameters that might be useful for general geochemical understanding

have been omitted from Table 3.5, because they may not be considered to be priorities for initial investigations.

One of the 'Suitability Indicators' (SI) devised by SKB is that DO should be absent at repository depth (see Table 2.2). This requirement originates from the knowledge that 'copper metal in water is not stable against oxidation in the presence of dissolved oxygen' (Puigdomenech and Taxén, 2000) and that the rate of corrosion of copper is lower in reducing than in oxidising conditions (Wersin et al., 1994; King et al., 2001). In the presence of oxygen, copper metal oxidises to cuprous (Cu^I) oxide, Cu_2O, which in turn oxidises further to form Cu^{II}, compounds, usually oxide and carbonate. Presence of these compounds as a protective layer on the copper surface passivates, at least partially, the metal against corrosion. pH/Eh predominance diagrams (known as Pourbaix diagrams) indicate that in pure water Cu_2O becomes stable at Eh values between about -200 and 0 mV, depending on temperature (100ºC and 25ºC respectively) (Puigdomenech and Taxén, 2000). However the thermodynamics of the Cu/Cu^+ reaction in pure water without O_2 indicates that 'copper does not corrode appreciably' in these conditions (Puigdomenech and Taxén, 2000).

At present, SKB intend to meet this requirement by showing that at least one of the proxy indicators Eh, Fe^{2+} or HS^- is indicative of absent DO. This, coupled with the 'let out' for the case where none of the indicators could be established reliably, is inadequate. The requirement should be to demonstrate that data for *both* DO and other redox indicators give consistent and indisputable evidence to meet the requirement and also to understand the relevant geochemical system which accounts for this property (this is similar to the 'function analysis' of Andersson et al. 2000). This means that all of the indicators should be measured, should be shown with a geochemical model to be internally consistent, and that their evolution should be understood.

The uncertainties that appear to be inherent in measuring DO should be taken into account in a cautious assessment of data from site investigation. The precautionary approach should be to demonstrate that DO is below a reasonable detection limit and then to consider the thermodynamic stability of Cu relative to O_2 at that detection limit value. The analytical detection limit for DO is, optimally, no more than 10 micrograms/l (Macalady et al., 1990; Langmuir, 1997). At 10 micrograms/l DO, the hypothetical Eh (i.e. determined by the $2H_2O \Leftrightarrow H_2 + O_2$ equilibrium, which differs from the actual measured Eh which is thought to depend on H_2O_2/O_2 equilibrium) would be +0.77V at pH 7 (Langmuir, 1997). This calculation carried out for both H_2O/O_2 and H_2O_2/O_2 redox couples is the basis for using Eh as a proxy for DO and for assuming that the requirement of Eh<0 mV is conservative. Conflicting with this degree of certainty, to some degree, is the knowledge that measured potentials at Eh electrodes are not represented by simple equilibria and thus may not be reliable indicators of presence/absence of DO.

The most robust way to approach this with respect to conditions at repository depth would be to make measurements systematically from the surface (i.e. from an environment which is known to be oxygenated). The technical difficulty of establishing 'zero' or absent DO would be met by demonstrating a trend of diminishing DO and decreasing Eh with increasing depth (Figure 3.1).
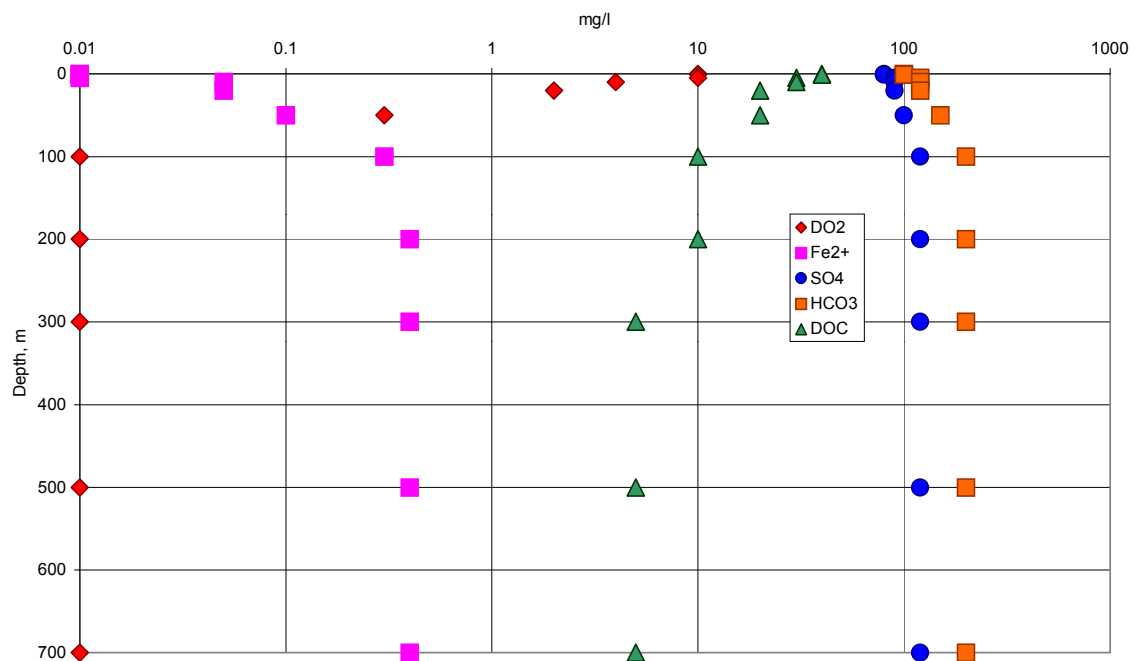

Figure 3.1. Schematic diagram showing the trends for dissolved oxygen, ferrous iron, sulphate, carbonate alkalinity, and dissolved organic carbon that should be measured to demonstrate confidence in the redox model for a groundwater system to repository depth.

This approach has already been demonstrated for groundwaters in the Whiteshell Research Area in Canada (Gascoyne, 1997) and also to some extent in the Redox Zone Experiment at Äspö (Banwart, 1995; Banwart et al., 1994). However data in Gascoyne (1997) also suggest that DO may be detectable when the Eh is negative: there is one case of 80 micrograms/l DO alongside Eh -75 mV, and general occurrence of 2-4 micrograms/l DO corresponding to Eh <-90 mV (Figure 3.2). These highlight the potential contention that could arise if SKB were to follow the present strategy. A proposed revision to the data requirement is summarised as:

o   DO, Eh and redox indicator species from surface to repository depth (both vertically and along flowpath to repository location);

o   Geochemical calculations demonstrating that redox indicators consistently support the absence of DO at repository depth and also support a model that DO is eliminated during transport to repository depth.
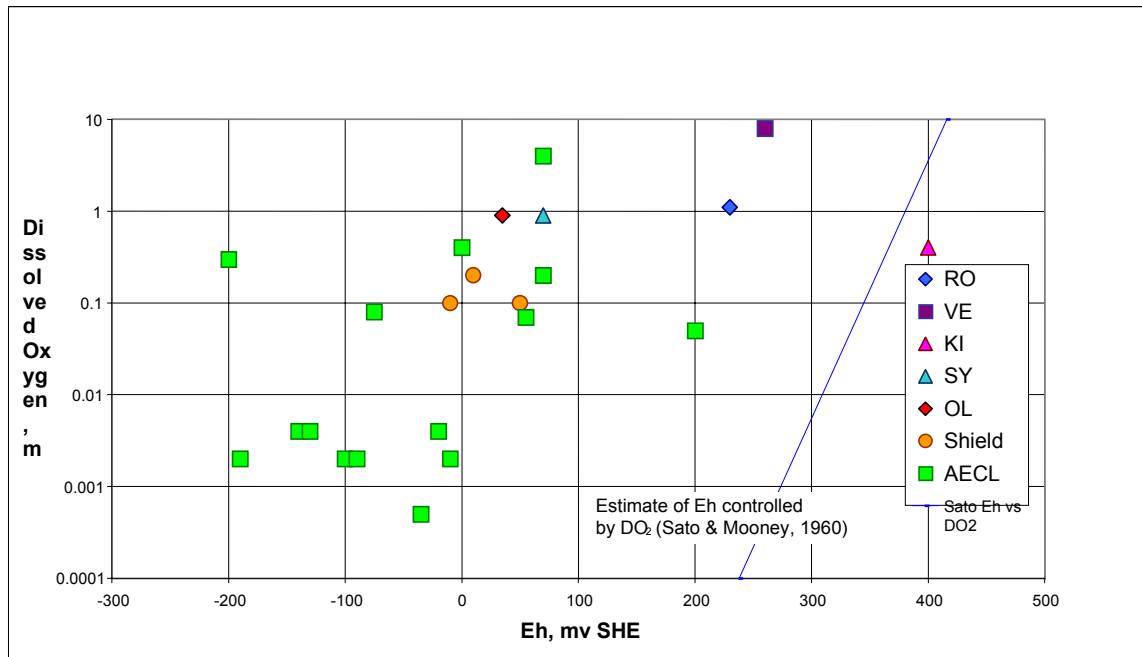
Figure 3.2   Eh versus DO for Fennoscandian and Canadian Shield groundwaters (from TVO 1982, Gascoyne 1997, Bottomley et al. 1990)

The findings in Banwart et al. (1994) and Gascoyne (1997) suggest that dissolved uranium (U) and Dissolved Organic Carbon (DOC) should be included as measured redox indicators. The implication of these requirements for site investigation strategy might be to place more weight on a specific investigation to achieve these targets, in place of general data acquisition as suggested in SKB (2000 and 2001). Moreover the sensitivity of these parameters to perturbation indicates that measurements should be carried out at an early stage of site investigation, probably in purpose-drilled boreholes at a variety of depths, starting shallow and progressing to greater depths.

SKB's Suitability Indicators also include a requirement that TDS is <100 g/l and a preference for the divalent cations $Ca^{2+}+Mg^{2+}$ being >4 mg/l (Table 1 and Andersson et al., 2000).   These are based by SKB on research conclusions that the swelling potential of bentonite is reduced when saturated with very saline water (Karnland, 1997) and that colloidal particles of bentonite might be re-suspended in extremely dilute solutions at the outer rim of the bentonite buffer (Laaksoharju et al., 1995b). An adequate scientific basis for setting these quantitative criteria for TDS and $Ca^{2+}+Mg^{2+}$ at the values proposed by SKB does not seem to be well established. Further evaluation of these requirements is recommended.

SKB's criteria should also include a limit for K^+ which is potentially significant as a sorbed cation that diminishes the swelling capacity of bentonite. The effect of K^+ on bentonite is considered in SR97 (SKB, 1999) and is dismissed as being insignificant although it is included as a preference for 'lower the better' values in Table 8-6 in SR-97 and is required to be <40 mg/l in Smellie et al. (1999). However K^+ sorbs to bentonite, without full illitisation taking place, and therefore participates in the same

18

cation exchange equilibria in which Na, Ca and Mg are also involved. Rather than the generic criteria, which are rather poorly supported as threshold values, a model of the effects of water chemistry, probably coupled with heat, on the mechanical performance of bentonite buffer is necessary. TDS and major cation parameters in Table 3.6 are a requirement for that model, as are reliable data for SiO_2, Al and pH.

Isotopic parameters are included in Table 3.5 because groundwater travel times should be an objective of initial site investigations. The approach at the initial stage should be to use data for ^{14}C, ^{3}H, stable isotopes and ^{4}He conjunctively to establish order-of-magnitude ages, or at least relative ages, for groundwaters at various depths and locations in the site. In addition to the commonly-used measurements such as ^{3}H and ^{14}C, other groundwater tracers such as chlorofluorocarbons (CFCs), sulphur hexafluoride (SF_6), thermonuclear and natural ^{36}Cl, and radiogenic ^{4}He should be used to maximise information. Sampling and analytical methods for these are well-established. A suggested approach would be to make measurements vertically and laterally (i.e. as a depth profile in a deep borehole plus shallow boreholes). Locations in the system where groundwater contents of ^{3}H and ^{14}C (and other indicators of young and old waters) fall below detection limit are significant, as are changes in the content of ^{4}He which can vary over orders of magnitude.

Groundwater ages inferred from isotopic data may be semi-quantitative model ages or even just qualitative or relative (as in the interpretation of stable O and H isotopes). They are the travel times for water or relevant solutes (e.g. HCO_3 in the case of ^{14}C in TIC) from recharge to the sampled point. Such data do not compare directly with the travel time of primary importance to safety, that is the travel time from repository to biosphere. It is suggested that groundwater age data has significance in two ways: (i) they should be used to test or calibrate hydrodynamic models of the site, and (ii) with cautious interpretation they indicate the overall rates of groundwater movement in a site and give at least a qualitative basis for comparing sites and candidate areas.

3.2.6 Chemical and Isotopic Compositions of Other Water Samples

Data are required for surface water sources (lakes, streams, springs) seawater (if relevant) and rainwater during the initial site investigation (Table 3.2). These are really part of the baseline data set. They provide important data to be included in the preliminary interpretation of the geochemistry of the site (Table 3.6). Seasonal variability in some parameters e.g. stable isotope ratios, may be significant and reliable temporal average compositions will be required. This will require monitoring of these baseline variations through seasonal changes over several years.

Surveying of ^{4}He flux at the surface through stream beds and other potential groundwater discharge areas could be a useful method for confirming qualitatively the magnitude of groundwater discharge from depth. This method has been used with successfully in the Canadian Shield (Sheppard et al., 1995). It is recommended that this method should be further evaluated.

Table 3.6 Parameters required from environmental water samples

Water source	Parameters and uses
Lakes and streams	Stable isotopes, salinity variation, major components, ^{4}He flux - identifying possible recharge or discharge to/from groundwater
Springs	Shallow groundwater suite of parameters, ^{4}He flux - source and age of discharging groundwater
Baltic seawater	As for lakes and streams, including Cl, Br, SO_4, stable isotopes - identifying intrusion of present or past seawater into groundwaters
Rainwater	Stable isotopes, major components - establishing seasonal variations in inputs to shallow groundwater

3.2.7 Compositions of Dissolved Gases

Gases dissolved in both shallow and deep groundwaters may provide useful information at the initial stage of site investigation. The priorities for data on dissolved gases are:

- O_2: DO, already discussed in Section 4.2.4;

- CH_4: indicator of reducing conditions and possible biological activity with sources of organic C;

- ^{4}He: radiogenic gas, cumulative product of radioactive decay of U and Th, indicator of groundwater age;

- CO_2: confirmation of pH-controlling carbonate equilibrium;

- CFCs: chlorofluorocarbons are a man-made global atmospheric containment and, like thermonuclear tritium, they are useful as indicators of the chronology and depth penetration of recent recharge in shallow groundwaters.

3.3   Complete Site Investigations

Detailed site investigations will have the aims of (SKB, 2000a):

o   Obtaining a geoscientific understanding of the site as regards current states and naturally ongoing processes;

o   Deriving a site-adapted repository layout;

o   Analysing the feasibility and consequences of the construction project;

o   Carrying out an assessment of long-term safety for the site.

The main products of the work will be descriptions of the site and of the facility, and a safety report. The safety report will be based on the methodology used in SR97 (SKB, 1999).

It can be assumed that the complete site investigations will involve the drilling of many more boreholes in addition to the smaller number in the initial site investigation. Some of these will be deep boreholes (i.e. to repository depth and below). There will be an extensive programme of hydraulic testing. Consequently the disturbance of geochemical conditions and the contamination with drilling water or testing water will increase, and the provenance of water samples will be less certain.

The value of having obtained a reliable set of geochemical parameters in the initial site investigation, in shallow and deep boreholes, will be evident. It is suggested that the expected levels of geoscientific understanding and of certainty in key parameters from the successive stages of site investigations should be:

o   Initial site investigations: fairly comprehensive geochemical interpretation of rocks, shallow groundwaters and baseline conditions, plus moderate certainty of deep geochemical conditions based on 'spot' measurements and on preliminary models for flow and geochemical processes.

o   Complete site investigations: sufficient understanding of geochemistry of rocks, minerals and groundwaters in the site and of groundwaters in surrounding region, including reliable data for geochemical parameters that directly affect safety.

Geochemical parameters and sample types required from complete site investigations are covered by the list in Table 3.2. However the emphasis is likely to shift towards improving the spatial resolution of geochemical information at repository depth (and below this), i.e. drilling, testing and sampling of more deep boreholes. However it is evident that a small number of reliable measurements for key parameters such as DO, redox and pH, is preferable to a larger number of measurements which have wide uncertainties due to contamination, mixing, provenance and other perturbations which may be prevalent in deep borehole samples. The desired outcome is data for key parameters for which a context has been established with the overall geoscientific understanding of the site.

The following sections describe the categories in Table 3.2 where more comprehensive geochemical testing will be required. Nevertheless work on other categories should be continued, as described in Section 4.1, to improve understanding of spatial and/or temporal variations and of processes. This should apply particularly to knowledge of the shallow groundwater system and of baseline conditions.

3.3.1 Chemical Compositions of Deep Groundwaters

A strategy needs to be developed for obtaining the most reliable samples and data, especially for unstable parameters such as DO, redox, ^{14}C, from deep boreholes. Changes of parameters for *undisturbed* deep groundwater conditions over the site investigation timescale would not be expected unless the system is subjected to a major perturbation such as a long-term pumping test or drawdown to an excavation as at the Äspö HRL. However the strategy should allow for more than one measurement of each required parameter at each sampling location, so that reproducibility of the value is demonstrated. This will of course require each sampling operation to be optimised to minimise contamination and other perturbations of the *in situ* parameter values.

Table 3.7   Additional geochemical parameters required from complete site investigation of deep groundwaters (i.e. these requirements should be added to the basic requirements already listed in Table 3.5).

Parameters	Geochemical interpretation
U & Th series nuclides	Isotopic disequilibrium in parent-daughter decay series, indicating water-rock reactions; comparison with natural analogues
^{36}Cl, ^{37}Cl/^{35}Cl	Salinity origin and residence time, analogue of source term radionuclide
I, Cs, Se, Sn, Zr	Analogues of source term radionuclides
REEs	Analogues for radionuclides an diagnostic of water-rock reactions
F, HPO$_4$, HCO$_3$	Complex formation with radionuclides
^{14}C(TOC), ^{13}C(TOC)	Groundwater age as transit time for soil-derived dissolved organic material
^{34}S/^{32}S in HS and SO$_4$, ^{18}O/^{16}O in SO$_4$	Sulphur geochemistry especially with respect to redox transformation and microbial activity
Dissolved CH$_4$ + H$_2$	Redox conditions, biological activity
Ne, Ar, Kr, Xe	Palaeorecharge temperatures from solubilities; support for palaeoclimate interpretation of stable O and H isotopes
^{40}Ar	Qualitative support for old groundwater ages
Colloid sizes and counts and identification	Potentially mobile particles, sorbing radionuclides
Microbial assemblage	Principal mediators for redox reactions and organic transformation, sources of biomass
^{11}B/^{10}B	Sources of saline groundwater

Additional geochemical parameters, supplementing the basic list of requirements that are in Table 2.1, that should be obtained for at least some of the deep boreholes are listed in Table 3.7. These two lists together are very similar to Table 8-2 in SKB Site Investigations 'Methods and General Execution Programme' (SKB, 2001b), except that rather more detail is given of the geochemical use of data. Some parameters for which the sampling and analysis are difficult and for which the interpretation is likely

to be very uncertain have been omitted (e.g. Xe isotopes). Some parameters have been added because they are considered to be of sufficient interest and are feasible analytically (e.g. $^{37}Cl/^{35}Cl$, Se, Sn, noble gases).

Si and Al are required for evaluating the state of chemical equilibrium between groundwater at repository depth and bentonite. pH and cation concentrations especially Na^+ and K^+ are also necessary for this calculation. There is some uncertainty about the thermodynamic parameters for bentonite and associated clay minerals in relation to cation contents, degrees of ordering, etc, but an estimation of the geochemical evolution of resaturated bentonite is nevertheless necessary. It is very unlikely that groundwater will be in equilibrium with bentonite, so there will be a tendency for the buffer to change, especially in the thermal environment of the near field. The factors that mitigate transformation of bentonite are, amongst others, supply of K^+ ion and the kinetics of the bentonite to illite transformation (Karnland et al. 2000).

U and Th series isotopes and their daughter nuclides in groundwaters are the products of release from sites in trace minerals and other hosts (e.g. calcite, iron oxides). The state of secular isotopic equilibrium in the decay series is diagnostic of the chemical equilibrium of U (Andrews et al., 1982). That knowledge would increase confidence in the interpretation of dissolved U concentrations as reliable indicators of redox conditions (e.g. Nordstrom and Puigdomenech, 1986; Smellie and Laaksoharju, 1992; Wikberg et al., 1992; Gascoyne et al., 1999). U and Th isotope ratios in groundwaters are also necessary data for interpretation of U isotopes in fracture minerals, e.g. calcites (Bath et al. 2000a).

^{36}Cl is now a routine parameter for investigation of groundwater dynamics and salinity sources. In the Stripa mine investigations, ^{36}Cl was distinctive for saline groundwaters that had flowed through different lithologies because of their different U contents and distinctive in situ isotope production characteristics (Andrews et al., 1986; Andrews et al., 1989b).

Similarly, but less conclusively, ^{36}Cl was one of several lines of evidence for the residence times of saline groundwaters in the basement rock system at the Sellafield site (Nirex, 1997a, 1997b; Metcalfe et al., 1999). Because there is a growing amount of evidence that the crystalline rock matrix may be a 'reservoir' for salinity (Gascoyne et al, 1992; Gascoyne et al., 1994), the state of in situ isotope production equilibrium may be an indirect diagnosis of the long-term stability of deep saline groundwaters in a fractured rock. Stable chlorine isotopes, $^{37}Cl/^{35}Cl$, is a more speculative measurement and may be diagnostic of processes of chloride exchange or movement. There is increasing evidence from $^{37}Cl/^{35}Cl$ that diffusion is the lower limit control for solute movements in lower permeability rocks, although this is much less evidence in crystalline rocks than in sedimentary rocks. There is a strong possibility in fractured rock groundwaters that it is diagnostic of mixing between groundwater masses with different sources of chloride (Frape et al., 1996).

Analyses of dissolved concentrations of trace elements I, Cs, Se, Sn, Zr should be required (in addition to the concentration of natural radionuclides U, Th, Ra, because these elements also occur as radionuclides in the waste inventory. There is an

expectation to understand the aqueous geochemistry and water-rock interaction of such elements. A similar case applies to the rare earth elements (REEs) because they have analogous geochemistry to the trivalent actinides (Miller et al. 1994).

F, HPO_4 and HCO_3 are of interest in groundwaters at repository depth because they are anions that form complexes with actinides. High concentrations could increase actinides solubilities. However the likely low range of concentrations in groundwaters makes these parameters of secondary importance for safety. Nevertheless they should be required to confirm that this is the case.

[14]C data for dissolved total organic carbon (TOC) are required to support the objective of dating groundwater travel times by conventional ^{14}C dating of dissolved inorganic carbon (TIC). The method is still a topic for research, especially in fractured rock groundwaters, but has been used at the Äspö HRL (Tullborg, 1997). The dominant form of TOC is fulvic acid, and ^{14}C contents of TOC sampled from shallow groundwaters are consistently higher than [14]C(TIC). This is as expected because [14]C(TIC) becomes diluted as the groundwater dissolves carbonate. Measurements of both [14]C(TIC) and [14]C(TOC) in very shallow groundwaters will provide 'initial' [14]C values for geochemical modelling of ^{14}C which is necessary to correct [14]C(TIC) interpretation for the effects of carbonate dilution. Modelling also requires $^{13}C/^{12}C$ values. The feasibility of ^{14}C dating of groundwater travel times, at least in shallow groundwaters, should be assessed with an appropriate number of ^{14}C measurements in both TIC and TOC. [14]C(TOC) is potentially a valuable check on [14]C(TIC) model ages that may be erroneously high if $^{13}C/^{12}C$ ratios are high in which case geochemical modelling may not be able to correct the ages reliably.

Dissolved CH_4 and H_2 data will add further to evidence for redox conditions and redox-controlling equilibria. Sulphur and oxygen isotopic ratios for the SO_4^{2-}/HS^- redox couple contribute to the understanding of that redox couple especially with respect to microbial mediation of the redox process.

Analyses of dissolved noble gases (Ne, Ar, Kr, Xe) are required to provide palaeorecharge temperatures that support the interpretation of stable O and H ratios. Examples where the combined noble gases and stable isotope data have increased confidence in the palaeoclimatic interpretation of water sources and ages are Stripa (Andrews et al., 1989c) and Sellafield (Nirex, 1997a, Bath et al., 1994). [40]Ar may provide qualitative support for [4]He and [36]Cl data in identifying very old groundwaters.

The abundances of colloids, data for their size-ranges, and identification of the solids involved (e.g. clays, organics or Fe-oxides) are required to assess whether colloidal sorption and transport of radionuclides could be a significant process.

In summary, it is proposed that SKI should expect the following objectives to be achieved by geochemical parameters obtained by SKB in the Complete Site Investigations:

o   Increased spatial resolution and reliability of site suitability criteria:
       - absence of dissolved oxygen and supporting redox data
       - salinity, pH, major cations, DOC, HS, etc

o   Geochemical model predictions for the stability of the bentonite buffer, simulating mineral equilibria and ion exchange for bentonite and trace mineral reactions

o   Geochemical model of DO attenuation and redox-controlling reaction from surface to repository depth, supported by data for aqueous redox couples, dissolved gases, mineral composition, TOC, U, S isotopes and microbial data

o   Estimates of travel times for water and solutes from recharge along flow lines to various depths from near-surface to below repository depth, based on an integrated interpretation of isotopic and noble gases data

o   Understanding of the evolution of groundwater compositions in terms of long-term flows and mixing with water-rock reactions, and demonstration of understanding with a forward model simulation of evolution of present system from past boundary conditions

o   Understanding of the geochemical distribution of natural radionuclides and of natural elements that also occur as radionuclides in source term inventory or are analogues of inventory radionuclides, in terms of water-rock reactions, release and retardation processes that will affect radionuclide mobilities and fluxes to biosphere.

4.   Sampling and Analyses

4.1   Rock and Mineral Compositions

Samples for petrographic and mineral studies and for analysing rock compositions will be taken from drillcores. The locations of boreholes from which drillcores should be obtained, and the numbers of samples analysed, are requirements that need further consideration. They will depend on the perceived geological heterogeneity of an area. Sufficient samples should be analysed to give an indication of the heterogeneity of composition in each relevant geological unit. The minimum to achieve this is likely to be three samples from different locations in each unit.   Adequacy of sample numbers will be determined by the requirements for reliable estimates for the ranges of parameters that are listed in Table 3.3.

A reasonable approach to numbers and distribution of analysed drillcore samples might be equally-spaced samples for each geological unit and sufficient number so that the standard deviation (or 2 x sd) of measurements for each petrographic or chemical parameters is less than the level of uncertainty that becomes significant in the geochemical interpretation. For example, if U concentration in rock is significant for modelling of in situ isotope production at a discrimination level of 10ppm, then

sufficient analyses should be done to give a sd value (or 2 x sd, for 95% confidence level) of ±10ppm.

Rock sample preparation techniques (i.e. acid dissolution and crushing for XRF powder mounts) and analytical methods should met criteria for blanks (i.e. background contamination), sensitivity (i.e. detection limits), precision (i.e. reproducibility of the whole procedure) and accuracy (i.e. calibration against certified standards). These should be adequate for purpose, but the principal requirement is that these are well documented so that reliability of data can be assessed.

Documentation of Quality Control (QC) measures should be required for all geochemical parameters.

Analytical methods should be capable of achieving adequate data resolution. Various instrumental methods may be employed (e.g. XRF, ICP-AES, ICP-MS, INAA) to meet this requirement. Specific methods will need to be adopted to analyse for some priority parameters to an adequate degree of reliability. The redox-buffering capacity of rock or mineral samples, specifically from fracture-filling material or wall-rock that is accessible by groundwaters, is one such set of data. Fe^{II}, Mn^{II} and sulphide mineral contents are required; Fe^{II} being most significant. In these cases, wet chemical analytical methods are likely to be employed – the classical method for Fe^{II} has recently been revised by Andrade et al. (2002).

Sampling of fracture-fill minerals for studies such as geochemical/isotopic analyses for palaeohydrogeology and sorption capacity requires special precautions to preserve representative material. Double- or triple-tube core drilling may be necessary to preserve such material from 'wash out' by drilling fluids. Sampling methods have been recommended in the EQUIP project (Bath et al., 2000). analytical methods for fracture minerals, as applied in fracture mineral studies in UK, Sweden, Finland and France have also been revised in the source report. Table 4.1 and the following paragraphs summarises the findings from that study.

Fracture minerals that are sampled for geochemical analyses and interpretations of water-rock equilibria should satisfy one or more of the following criteria:

- o Identified petrographically as the youngest mineralisation;

- o Spatially-associated with present groundwater flow;

- o Adjacent to zones with high hydraulic conductivity;

- o Petrographic evidence for in situ open porosity;

- o Poorly crystalline low temperature phases.

The locations of samples should be recorded with assessments of the above criteria, and should be able to be correlated with relevant hydrochemical data preferably from the same location.

Table 4.1   Comparison of advantages and disadvantages of different drilling techniques for recovery of fracture infills and other samples (adapted from Bath et al., 2000).

Method	Drilling fluid	Advantages	Disadvantages
Single barrel (56-65mm)	Water	No contamination of formation waters	Poor preservation of minerals, abrasion of open fracture surfaces
Single barrel (75-100mm)	Bentonite/ polymer)	Good recovery and preservation of mineral fabrics	Contamination of formation water and minerals by mud and trace additives
Triple barrel (56-95mm)	Water	Good preservation of minerals fabrics and minimal abrasion. No contamination of formation waters	Difficult drilling poor boreholes stability in some lithologies, reduced core recovery in some lithologies
Triple barrel	Mud (Bentonite/ polymer)	Very good core recovery and preservation of mineral fabrics, minimal abrasion of fracture surfaces	Contamination of formation waters, mud coating on open surfaces

The following methods for petrographic, mineralogical and geochemical characterisation of secondary minerals should be considered (Bath et al., 2000):

- SEM or low-vacuum SEM of stub mounts of fragments (± back-scattered electron imaging, BSE).

- Energy-dispersive X-ray analysis (EDXA) during SEM observation.

- Petrographic microscopy examination of polished thin sections and wafers for fluid inclusions (delicate fabrics should be preserved by epoxy-resin impregnation or similar methods).

- BSEM, EDXA and cathodoluminescence (CL) examination of thin sections; Cl can be based on optical microscopy or on SEM, but cold-cathode optical CL microscopy has been shown to be better for calcite.

- Fluid inclusion distribution and abundances should be related to microstructural markers, e.g. fluid inclusion planes and microfissures, to assist in interpreting their relative chronologies and relationships to groundwater flow paths.

- Microchemical analyses of mineral grains, and of compositional zones within grains, using electron probe microanalyses (EPMA) at locations identified by CL or SEM images; wavelength-dispersive EPMA should be able to achieve detection limits of about 1000ppm whereas energy-dispersive EPMA is about 10x less sensitive.

- Microchemical analyses and isotopic analyses are now also possible by laser ablation analysis, using ICP-MS spectrometry for analyses of major and trace elements and some isotope ratios and gas source mass spectrometry for stable oxygen and carbon isotope ratios. LA-ICP-MS can achieve a detection limit around 1ppm.

- Stable oxygen and carbon isotope ratios can also now be measured by ion microprobe at micro-scale resolution and with better precision than is possible by laser ablation mass spectrometry.

- Microthermometry and LA-ICP-MS analyses can be used to characterise individual fluid inclusions for formation temperature and chemical composition, though detectio limits and precision of chemical analyses are rather poor.

It should be a requirement that all analyses in the above categories are reported with adequate calibration and evaluation of precision to allow comparison of data from different methods (e.g. mineral compositions by LA-ICP-MS and EDXA, or water compositions in fluid inclusions and groundwater samples).

4.2   Groundwater Compositions

4.2.1 General Sampling Strategy

Obtaining groundwater samples that are representative of in situ chemical conditions at a given location in a fractured rock is a major technological and scientific challenge. It is rarely achieved with total success. An appropriate requirement is therefore that the sampling strategy should optimise the opportunity to measure key parameters with high reliability. Sampling strategies and the quality of water samples are discussed in Laaksoharju et al. (1993) and Laaksoharju (1999). Measures that can be used to improve reliability of water samples include:

o Sampling during drilling or as soon as possible after completion of a borehole;

o Use of a tracer in drilling water;

o Pumping to achieve minimal contamination (but mixed water may be sampled after prolonged pumping);

o Drilling and sampling in a 'hydrochemical' borehole that is dedicated to optimising sampling;

o Deployment of pressurised water samplers, pumping water to a surface-based flow-through electrode monitoring system, or use of a downhole tool for making electrode measurements;

o Completion of boreholes with sampling lines in packered intervals or in multi-level sampling systems (e.g. Westbay);

o Choice of drilling fluid based on chemical considerations, e.g. water, organic polymer mud or bentonite mud.

It should be a requirement that data for groundwater chemistry should be reported with information about the application of these measures in acquiring data. Selection of the most reliable values for parameters, with associated ranges of uncertainty, could then be carried out using a quality scoring method or other objective methods (e.g. Laaksoharju, 1999; Nirex, 1997).

4.2.2 Frequency of Samples

Sampling frequency for groundwaters is a potentially contentious issue for site investigations, especially where groundwater compositions are expected to be heterogeneous. A conceptual model of hydrochemical variability is desirable at the preliminary stage of desk study. This will guide the optimal frequency of sampling, aiming for both adequate knowledge of variation and minimal disturbance of the site. The required density of sampling and thus of information will also depend on how data will be used. If data for conservative (i.e. non-reacting) solutes and isotopic ratios (e.g. Cl, Br, $\delta^{18}O$, δ^2H, ^4He) will be used to describe the distribution of water types over the mesh of a groundwater flow-transport model, then data density will need to be higher than otherwise. Referring to the indicative compositions of reference waters in Table 3.1 and more generally at Äspö (Laaksoharju et al., 1999a), it is possible to estimate that, for example, ±400 mg/l Cl represents an error of about 10% in resolving the proportions of meteoric and Baltic waters in a groundwater from mixed sources. Similarly, ±1‰ $\delta^{18}O$ represents a 10% error in resolving proportions of meteoric and glacial waters in a mixed groundwater. Thus it can be suggested that, for populating the mesh for calibrating a flow-transport model, the lateral and vertical sample distribution should be adequate to acquire data representing changes of about ±400 mg/l Cl or ±1‰ $\delta^{18}O$. To some extent, the sample distribution can be reduced by interpolation and expert judgement.

4.2.3 Analyses of Groundwater Samples

A range of analytical methods can be used to measure the required parameters listed in Tables 3.4 and 3.6. Labile parameters such as pH, Eh, DO and alkalinity must be measured in the field, possibly with a downhole probe for pH and Eh, using electrodes or titration methods. Other redox-sensitive parameters, in addition to DO and Eh, also should be measured under controlled conditions at the time of sampling, or the 'in situ' distribution of species (e.g. in the Fe^{2+}/Fe^{3+} or HS^-/SO_4^{2-} systems) should be preserved for later analysis. Data for these parameters should be reported with information about the precautions taken to preserve in situ conditions. Calibration is necessary, especially for Eh and zero DO, and it is also essential that Eh values are reported explicitly with respect to the appropriate reference electrode. Alkalinity may be difficult to analyse reliably, especially in saline groundwaters in which alkalinity is low. The 'Gran' potentiometric titration method may be better for achieving a reliable end point in these cases. Carbonate alkalinity should be corrected for non-carbonate alkalinity due to Si and B.

Instrumental methods are likely to be used for most of the major and trace cation and anion analyses. The methods may include AAS, ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy), ICP-MS (Inductively-Coupled Plasma source Mass Spectrometry, and IC (Ion Chromatography). However other methods may be more appropriate for some analytes and these should be considered where appropriate: 'classical wet chemistry' methods such as gravimetry or titration (e.g. for Cl, SO_4), flame spectrophotometry (e.g. for Li, Na, K), IR auto-analyser (for TIC and TOC), and ion-selective electrode (e.g. for F). Because of its importance for understanding redox conditions, attention should be given to obtaining meaningful analyses of ionic species of iron in both oxidation states (e.g. direct analysis of Fe^{III}; Bangthanh To et al., 1999). Methods should be chosen to be optimal for the particular solution compositions. Calibration should also optimise data accuracy, using matched standards as necessary for calibration.

5.   Interpretation Tools

In only a few cases are values of geochemical parameters used directly in an assessment of repository safety and long-term performance. The SKB programme has identified these parameters as 'Suitability Indictors' (Table 2.2). For the majority of geochemical parameters, however, processing and interpretation are necessary before the significance of measured data can be realised. The Suitability Indicators also need to be understood, and confidence to be built in their validity, by means of a 'function analysis', as explained in Section 2.1.

The tools that are used to carry out data processing, interpretation and function analysis can be described in a number of categories:

o   Graphical tools for data visualisation,

o   Normative calculations of mineral compositions or rocks,

o   Data analysis tools using statistical methods,

o   Speciation models of aqueous solutes,

o   Water-rock equilibrium and mass transfer models,

o   Coupled models of groundwater flow, mass transport and reaction,

o   Carbon-14 groundwater age correction models,

o   In situ isotope production models,

o   Radionuclide complexation and geochemical exchange models.

Some of these tools are discussed briefly in the following sections. However the requirements that SKI might expect to be satisfied by SKB in these respects beyond the scope of this report and should be explored in more detail in a future report.

5.1   Tools for Data Visualisation and Analysis

These tools include the conventional, widely-used, graphical methods such as Piper plots, Durov diagrams, Stiff plots and Schoeller diagrams. One or more of these might be used as a preliminary illustration of data variation and trends, though they have limited value in a qualitative sense. No particular requirements are envisaged in this respect.

Statistical analysis can be used to simplify variation in multi-parameter data sets and to identify key factors that govern data variability. In the case of hydrochemical data for compositions of water samples, statistical analysis can be used to identify

components that make up individual samples. Principal component analysis (PCA) is the most common statistical method, and has been developed by SKB in the 'M3' computer code (Laaksoharju et al, 1999a, b; Laaksoharju, 1999).

M3 is the abbreviation for Multivariate Mixing and Mass balance calculations and is a computer code that, in conjunctive use with a visualisation package such as Voxel Analyst, offers convenient visualisation of compositional variations in groundwaters (Laaksoharju et. al., 1999b). It allows the major compositional features of waters to be projected onto a 2D plot and thus provides a means of illustrating composition variations on a single diagram. The M3 plot is a cross-plot of the two dominant PCs and illustrates compositional variations and mixing between putative end-members or reference waters.

The M3 approach consists of four main steps. The first step is a principal component analysis of the measured compositions (i.e. data for the major solutes Cl, Ca, Na, Mg, K, SO_4 and HCO_3 and isotopes δ^2H, $\delta^{18}O$ and ^3H) of the groundwater samples. PCA consists essentially of seeking new coordinate axes (directions of principal components) such that the spread of the projection of the cloud of points corresponding to the samples onto the first new axis is as large as possible. The second step is to identify a small number of reference waters. This is done on the basis of the M3 plot, supported by physical and geochemical understanding of the groundwater flow system at the site of interest. The reference waters should form the corners of a polygon in the M3 plot, and should correspond to water compositions that have physical and geochemical significance for the site. The reference waters are not uniquely determined by the scatter plot, but depend, to some extent, on the judgment of the analyst.

The third step in the M3 approach is to determine how each sample might be constituted as a mixture of the reference waters. If there are only three reference waters, then this can only be done in one way, for example in interpretation of groundwater mixing at the Oklo natural analogue site (Gurban et al., 1999). In this case, the fraction of each reference water in the mixture is given by the ratio of the area of the triangle whose corners correspond to the two other reference waters and the sample to the area of the triangle whose corners correspond to the reference waters.

However, if there are more than three reference waters, then the mixing fractions are not uniquely determined. In order to deal with this potential ambiguity, the point in the M3 plot corresponding to a mixture of the reference waters in equal proportions is determined and essentially acts as an additional reference water in calculating mixtures. This introduces an artefact into the mixing model that adds uncertainty to the estimated proportions of reference waters. Four or five reference waters have been deduced for the groundwaters at Äspö and four reference waters for groundwaters at the Whiteshell Research Area in Canada (Laaksoharju et al. 1999a; Laaksoharju et al. 2000). The uncertainty in mixing proportions was estimated to be ±0.1 (Laaksoharju et al. 1999b), although the uncertainties in interpretations for individual water samples could be significantly larger.

In new site investigations, the extent to which the M3 approach is valid should be considered, because uncertainties in these cases might be much larger than the uncertainties quoted above. For example, the approach may be less effective at a 'freshwater' site at which groundwater salinity covers a smaller range. At such a site, more than two principal components may be needed to give a reasonable description of the variability in the composition of groundwater samples. There is also uncertainty in estimating mixing fractions from an M3 plot which has been constructed using data for reactive solutes as well as the non-reactive 'conservative' species.

The fourth step in the M3 approach is to determine, for each groundwater sample, the deviations of the concentrations of the various groundwater constituents from the values that they would have as a result of mixing the reference waters in the fractions given by the calculated mixing fractions. These deviations are interpreted as the result of reactions in Laaksoharju et al. (1999a), although there are other possibilities to explain such deviations and it is considered that this method of interpreting geochemical reactions may not be reliable. If the M3 method is used in this way to infer water-rock reactions, a full discussion of uncertainties and alternative interpretations should be required.

The M3 approach is simple to implement but should not be used as a 'black box' tool for deducing and quantifying mixing between groundwater masses. It involves some degree of 'expert' interpretation in the choice of reference waters although the core of the method is an objective analysis of data. This has advantages and disadvantages, and depends on the hydrochemistry of the site. Overall, quantitative mixing interpretations from M3 should be regarded with caution though this or other statistical methods are generally useful as tools for processing large multi-parameter hydrochemical data sets to visualise the spread of water compositions and to identify the end-members involved in mixing.

5.2   Tools for Geochemical Speciation and Modelling

Geochemical modelling tools that calculate ionic speciation and equilibria with solid phases are widely used and accepted. The computer codes that are most widely used are PHREEQC (Parkhurst, 1995) and EQ3/6 (Wolery et al., 1990). Information that should be available for reference when these codes are used in the interpretation of site investigation data includes:

- o   Thermodynamic data base (TDB) for ionic species in solution and for mineral phases;
- o   Mineral phases and complex ions that are included in the model;
- o   Sub-models and parameters that are implicit in the model for solid solutions, ion exchange equilibria on mineral surfaces, etc;
- o   Activity coefficient calculations, including the uncertainties due to the ionic model for high ionic strength solutions, i.e. whether the Pitzer approximation is used;
- o   Sub-models, and assumptions involved, in modelling redox equilibria and pH-controlling equilibria.

Uncertainties in the TDB are, in general, less significant than are uncertainties arising from the particular sub-models and assumptions that might be implicit in a modelling approach.   Of specific importance in the present considerations is the method that is used to compare the redox indicators, including dissolved oxygen (DO). The 'Sato formula' has been used to relate pO_2, pH and Eh, but this involves various assumptions and is of doubtful quantitative validity (Langmuir, 1997). The other redox-sensitive equilibria, for example, those involving HS/SO_4^{2-}, Fe^{2+}/Fe^{3+}, and NH_4^+/NO_3^- probably have dominant uncertainties originating in the analytical data for the subordinate species in each case, i.e. HS^-, Fe^{3+}, and both NH_4^+ and NO_3^-. Information about these uncertainties should be required, with an estimation of how they propagate into uncertainty in the derived Eh value.   The same types of uncertainties occur in the data that represent pH-controlling equilibria, specifically carbonate and aluminosilicate mineral dissolution equilibria. For understanding the rôle of the carbonate system in controlling pH, pCO_2 should be measured independently and then reconciled with the measured pH and alkalinity.

5.3   Tools for Modelling of Environmental Isotope Systems

Environmental isotopes may provide useful information about groundwater ages and solute residence times. Raw isotopic data e.g. for ^{14}C, ^{36}Cl, have to be interpreted by means of radioactive decay equations and models for their geochemical evolution in relation to the relevant stable isotopes i.e. ^{13}C and ^{35}Cl. Geochemical models for these isotope systems have substantial uncertainty associated with them, arising from the need for supporting data and also from the range of possibilities that are inherent in the conceptual models.

The geochemical model for calculating groundwater ages from ^{14}C data makes the basic assumption that residence times of dissolved inorganic carbon (DIC) or organic carbon (DOC) are related to groundwater movement. ^{14}C entering the groundwater system at recharge (as DIC) is diluted by carbonate reactions and/or DOC-oxidation. These processes can be simulated by a geochemical model from which a 'correction' to the ^{14}C age can be estimated. Information that should be required in support of these 'model age' calculations includes:

- o Geochemical conceptual model for C-isotope evolution, including consideration of various alternative concepts;
- o Calculations to evaluate the consistency of various C-isotope evolution models with hydrochemical data along flow lines (there are various calculation tools available for this, including the NETPATH computer code);
- o Stable C-isotope ($^{13}C/^{12}C$) analyses of relevant reactive species and components of DIC evolution, namely DIC at the point of recharge and in relatively young groundwaters that are at or close to carbonate equilibrium and solid carbonate mineral phases that can react with groundwaters (e.g. the most recent generations of fracture-fill calcite).

The latter data requirement is particularly important for satisfactory C-isotope modelling and is often omitted from investigations that acquire ^{14}C data. In the SKB investigations, obtaining ^{14}C data without these supporting data would result in an incomplete and inadequate interpretation.

The geochemical model for interpreting ^{36}Cl measurements requires the in situ production of ^{36}Cl within the host rocks to be evaluated. This is done by calculating the natural neutron flux originating from (α, n) reactions and then calculating the rate of ^{35}Cl to ^{36}Cl conversion by knowledge of the relevant cross-section for that nuclear reaction. Parameter requirements for the calculation include:

- o U and Th plus Li contents, that account for production of neutrons by (α, n) reactions;
- o Concentrations of neutron-absorbing elements (B, Ge, etc) that attenuate the neutron flux;
- o Cl concentration in rock matrix where in situ production is most likely.

The in situ $^{36}Cl/^{35}Cl$ using these parameters is compared with the measured ^{36}Cl content to infer the residence time of chloride ion in relation to the time for isotopic secular equilibrium to be achieved. It has to be remembered that the flow path along which sampled chloride has evolved should, ideally, be geochemically characterised. In practice this is not possible and the uncertainty attributed to the interpretation should be estimated with some knowledge of the geochemical heterogeneity along the flow path.

Other environmental isotope data also require either geochemical or palaeoclimatic context data to support interpretations. Stable oxygen and hydrogen isotope data ($^{18}O/^{16}O$ and $^2H/^1H$) that are used to attribute 'cold climate ages' to groundwaters

should be supported by palaeoclimate information and relevant temperature coefficients for the isotope ratios; in addition other factors such as altitude effects and palaeogeographical effects on water compositions need to be taken into account. Dissolved noble gas concentrations (Ne, Ar, Kr, Xe) are an additional test for recharge temperature variations.

If the hydrodynamic interpretations of shallow groundwaters are calibrated by data for cosmic-ray produced and/or anthropogenic isotopes and other tracers of recent recharge (e.g. ^{3}H, ^{85}Kr, ^{36}Cl, CFCs), then the measured data need to be supported by as much information about past and present inputs of these species. As mentioned previously, the most simple and incontrovertible interpretation of such data would come from the demonstration of depth ranges below which anthropogenic or 'geologically-recent' inputs are absent and only in situ naturally-produced isotopes are found.

6. Conclusions

The geochemical parameters that are required from SKB's forthcoming investigations in Oskarshamn, Östhammar and Tierp municipalities have been reviewed. The starting point has been SKB's own documentation that specifies the properties of the host rock that are required by the KBS-3 repository concept and the parameters that need to be measured by site investigation to evaluate these properties (Andersson et al., 1998, 2000; SKB, 2000a, 2001b). SKB have established a number of geoscientific suitability indicators that they intend to assess against quantitative criteria to determine whether there are properties that exclude a site from further consideration. In addition, preferences are stated for the ranges of some properties, implying that these have some particular rôle in considering the geoscientific attributes of sites. However the suitability indicators on their own cannot be used to decide that a repository would be safe – that can only be carried out by a comprehensive safety assessment.

Amongst the suitability indicators, quantitative requirements are defined for the dissolved oxygen contents, pH and salinity (as TDS) of groundwaters at proposed repository depth. Preferred ranges for a few other parameters have also been defined by SKB, and in addition an extensive list of measurements has been specified to provide geoscientific understanding. 'Function analyses' are also identified as having an important rôle; essentially these are geochemical models for particular parameters that link them with other measurements and could be used to test for consistency and to define them more reliably.

The review concludes that this framework for planning site investigations is logical and generally thorough. In one sense, it is rather over-prescriptive in setting up quantitative suitability criteria. A notable omission from the planned measurements is dissolved oxygen (DO) even though it is identified as one of the primary suitability criteria, with a stated requirement to be zero. Presumably it is omitted because of practical difficulties in confirming zero DO by direct measurements. Instead, it addresses this issue with 'proxy' measurements of redox and by using function

analysis. Whilst agreeing that this approach is geochemically sound, it should not obviate the need to demonstrate by direct measurement that the primary parameter is as it should be. This issue illustrates the importance of planning the site investigations to make all necessary measurements with optimum and consistent accuracy and precision, and to present these with a context of fully understanding sources of remaining uncertainty and bias.

A potential weakness of the suitability criteria is that they have varying degrees of robustness as quantitative limits. The choice of the stated limits is not consistently well-supported by underlying research in every case, for example in choices of criteria for salinity and cation concentrations of groundwater with respect to bentonite performance and long-term stability. Whilst the simplicity and transparency of these quantitative criteria are desirable, their credibility should be able to stand up to critical review. Moreover, they are of limited or no value if the limits set would be invariably achieved in any site, thus giving the misleading impression that all sites might be suitable.

The lists of parameters and attributes that will be measured for the more general objective of geoscientific understanding, i.e. understanding the processes and evolution in a site, are fairly exhaustive in terms of groundwater chemistry parameters although there are some omissions and also some dubious items in the list. Some complementary measurements on rock and mineral samples and on waters and gases in shallower groundwaters are also required. For example, obtaining samples of fracture minerals and of groundwaters that co-exist with the minerals will provide a higher quality of interpretation and understanding than if the sampling were to be uncoordinated. Another example is the potential value of measuring helium in shallow groundwaters, surface seepages and in soil gases to help in identifying discharges of deep groundwater circulation.

Two themes for geochemical data acquisition have been suggested in this review. Firstly, it is proposed that all parameters to be measured should be supported from the start by a clear idea of how they will be used, how well they need to be measured, and what the implications of various values and uncertainties might be. This approach underpins how the 'parameter requirements' should be set up, and it also aims to achieve a consistent approach to the practicalities of getting usable and reliable data. To some extent, this has been addressed by SKB in Laaksoharju (1999). Two examples illustrate how this principle should be implemented. The first example is obtaining a comprehensive hydrochemical data set that will be adequate for full geochemical modelling of bentonite stability. The second example is measuring complementary sets of isotopic, dissolved gas and hydrochemical data that will give the best possible interpretation of groundwater and solute ages at various points in the geosphere. A related issue is the necessity of obtaining the best possible water samples and analyses in the initial stage of the investigation. It would be prudent to assume that the earliest groundwater samples (including samples taken during drilling) are potentially the most significant and most representative. The procedures for borehole drilling and testing should take this into account.

The second theme is that sufficient effort should go into obtaining geochemical data for shallow groundwaters, i.e. between about 50m and 300m depth, in addition to targeting deeper groundwaters in the range of repository depth. The rationale for this is two-fold: that understanding groundwater movements and compositions at shallower depths is necessary for understanding the deeper regime and its recharge, discharge and mixing, and that confidence about the interpretation of geochemical and isotopic data in these more active groundwaters is a prerequisite for reliably interpreting data for deeper groundwaters. For some of the key parameters such as dissolved oxygen, redox, salinity and isotopic data, vertical profiles from the surface to depth, and sequences along flow lines, are much more meaningful than isolated spot measurements which might have poorly defined reliability.

In addition to the immediate issues of geochemical data acquisition are the equally important issues of data interpretation and geochemical modelling. SKB's parameter specifications do not emphasise the importance of interpretation tools and geoscientific context and comparisons, although methodologies have been presented and discussed by SKB in other documentation (e.g. Laaksoharju, 1999). Whilst a few geochemical parameters are directly applicable to performance of the near-field system, most other geochemical data have significance to long-term safety only when secondary information (such as long-term flow directions and mixing, groundwater ages, and mineral-water reactions and ion exchange equilibria) can be deduced by interpretation. The reliability of these inferences depends on the calculation tools used, the geochemical concepts (and the possibility of alternative concepts) and on the extent of supporting research and comparable investigations. The requirements in terms of supporting data and interpretation tools, and the interrelationships between them, need further consideration.

In conclusion, it can be seen that geochemical aspects of site investigations are a complex set of parameter requirements that create challenges in reconciling their priorities versus other testing activities, successful sampling, and interpreting data for use in making safety judgements. This review has attempted to identify most of the issues and to point to requirements and potential difficulties. Further work is required to address some of the issues to avoid there being omissions or unexpected difficulties as the site investigations proceed.

7. Bibliography

Andersson, J. Almén, K-E, Ericsson, L.O., Fredriksson, A., Karlsson, F., Stanfors, R. and Ström, A. (1998) Parameters of importance to determine during geoscientific site investigation. Technical Report TR-98-02. SKB Stockholm.

Andersson, J., Ström, A., Svemar, C., Almén, K-E and Ericsson, L.R. (2000) What requirements does the KBS-3 repository make on the host rock? Geoscientific suitability indicators and criteria for siting and site evaluation. Technical Report TR-00-12. SKB Stockholm.

Andrage, S., Hypolito, R., Horstpeter, H.G., Ulbrich, J. and Silva, M.L. (2002) Iron (II) oxide determination in rocks and minerals. Chemical Geology, 182, 85-89.

Andrews, J.N., Giles, I.S., Kay, R.L.F., Lee, D.J., Osmond, J.K., Cowart, J.B., Fritz, P. Barker, J.F. and Gale, J. (1982) Radioelements, radiogenic helium and age relationships for groundwaters from the granites at Stripa, Sweden. Geochimica et Cosmochimica Acta, 46, 1533-1542.

Andrews, J.N., Fontes, J.-Ch., Michelot, J.-L and Elmore, D. (1986) In-site neutron flux, ^{36}Cl production and groundwater evolution in crystalline rocks at Stripa, Sweden. Earth and Planetary Science Letters, 77, 49-58.

Andrews, J.N., Ford, D.J., Hussain, N. Trivedi, D. and Youngman, M.J. (1989a) natural radioelement solution by circulating groundwaters in the Stripa granite. Geochimica et Cosmochimica Acta, 53, 1791-1802.

Andrews, J.N., Davis, S.N., Fabryka-Martin, J. Fontes, J-Ch., Lehmann, B.E., Loosli, H.H., Michelot, J-L., Moser, H., Smith, B. and Wolf, M. (1989b) The in situ production of radioisotopes in rock matrices with particular reference to the Stripa granite. Geochimica et Cosmochimica Acta, 53, 1803-1815.

Andrews, J.N., Hussain, N. and Youngman, M.J. (1989c) Atmospheric and radiogenic gases in groundwaters from the Stripa granite. Geochimica et Cosmochimica Acta, 53, 1831-1841.

Bangthanh, T., Nordstrom, D.K., Cunningham, K.M., Ball, J.W. and McCleskey, R.B. (1999) New method for the direct determination of dissolved Fe(III) concentration in acid mine waters. Environmental Science and Technology, 33, 807-813.

Banwart, S., Gustafsson, E., Laaksoharju, M., Nilsson, A-C., Tullborg, E-L. and Wallin, B. (1994) Large-scale intrusion of shallow water into a vertical fracture zone in crystalline bedrock: initial hydrochemical perturbation during tunnel construction at the Äspö Hard Rock Laboratory, south-eastern Sweden. Water Resources Research, 30, 1747-1763.

Bath, A.H., McCartney, R.A., Richards, H.G., Metcalfe, R. and Crawford, M.B. (1994) Groundwater chemistry in the Sellafield area: a preliminary interpretation. In The Geology and Hydrogeology of the Sellafield Area, Proceedings of the Nirex Seminar. Quarterly Journal of Engineering Geology, 29, supplement 1, ppS39-S59.

Bath, A., Milodowski, A., Ruotsalainen, P., Tullborg, E.-L., Cortés Ruiz, A. and Aranyossy, J.-F. (2000a) Evidence from Mineralogy and Geochemistry for the Evolution of Groundwater Systems During the Quaternary for Use In Radioactive Waste Repository Assessment (EQUIP Project). Final Report, Contract No FI4W-CT96-0031. Euratom/EC-DG-Research, Report EUR 19613EN. 157pp. European Commission, Luxembourg.

Bath, A.H., Boulton, G., Marivoet, J. and Blomqvist, R. (2000b) What Approach and Tools Do We Have for Understanding the Past Evolution of Groundwater Systems as a Guide to Future Evolution for Repository Performance Assessment? In Euradwaste 1999 'Radioactive Waste Management Strategies and Issues' (C. Davies, ed), Proc. Conference Luxembourg, November 1999. CEC Report EUR 19143EN, pp 257-273. EC Luxembourg.

Bruno, J., Duro, L., and Grivé, M. (2001) The applicability and limitations of the geochemical models and tools used in simulating radionuclide behaviour in natural waters. Lessons learned from the Blind Predictive Modelling exercises performed in conjunction with Natural Analogue studies. Technical Report TR-01-20. SKB Stockholm.

Clark, I., Douglas, M., Raven, K. and Bottomley, D. (1999) Tracing surface-to-depth flow and mixing at the Con Mine, Yellowknife, Canada: an analogue for the hydrogeology of radioactive waste repositories. Proceedings of International Conference on the Study of Environmental Change Using Isotope Techniques. IAEA-SM-361/42, pp92-93. IAEA Vienna.

Clauer, N., Frape, S.K. and Fritz, B. (1989) Calcite veins of the Stripa granite (Sweden) as records of the origin of the groundwaters and their interactions with the granite body. Geochimica et Cosmochimica Acta, 53, 1777-1781.

Collon, P., Kutschera, W., Lehmann, B.E., Loosli, H.H., Purtschert, Love, A., Sampson, L. Davids, B., Fauerbach, M. Harkewicz, R., Morrissey, D., Sherrill, B., Steiner, M., Pardo, R. and Paul, M. (1999) Development of Accelerator Mass Spectrometry (AMS) for the detection of ^{81}Kr and first application to groundwater dating. Proceedings of International Conference on the Study of Environmental Change Using Isotope Techniques. IAEA-SM-361/18, pp42-43. IAEA Vienna.

Cramer, J. and Smellie, J. (eds) (1994) Final Report of the AECL/SKB Cigar Lake Analogue Study. Technical Report TR-94-04. SKB Stockholm.

Douglas, M., Clark, I.D., Raven, K. and Bottomley, D. (2000) Groundwater mixing dynamics at a Canadian Shield mine. Journal of Hydrology, 235, 88-103.

Frape, S.K., Bryant, G., Blomqvist, R., and Ruskeeniemi, T. (1996) Isotopes in Water Resources Management. Proceedings of a Symposium on Isotopes in Water Resources Management, Vienna, 20-24 March 1995. Volume 1, pp19-30. IAEA Vienna.

Gascoyne, M. (1997) Evolution of redox conditions and groundwater composition in recharge-discharge environments on the Canadian Shield. Hydrogeology Journal, 5, 4-18.

Gascoyne, M. and Chan, T. (1992) Comparison of Numerically Modelled Groundwater Residence Time with Isotopic Age Data. In Palaeohydrogeological Methods and their Applications, Proceedings of an NEA Workshop, Paris, France, November 1992, pp199-218. Nuclear Energy Agency of the OECD, Paris, France.

Gascoyne, M., Kamineni, D.C. and Fabryka-Martin, J. (1992) Chlorine-36 in groundwaters in the Lac du Bonnet granite, south-eastern Manitoba, Canada. In WRI-7, Proc. 7th Intl. Symposium on Water-Rock Interaction, Park City, USA, July 1992. (Y. Kharaka & A. Maest, eds) p931. Balkema, Rotterdam.

Gascoyne, M., Sharma, P. and Kubik, P.W. (1994) Origin of groundwater salinity in the Lac du Bonnet granite, south-eastern Manitoba, from ^{36}Cl measurements. Nuclear Instruments and Methods in Physics Research B92, 389-392.

Gascoyne, M., Ross, J.D. and Watson, R.L. (1996) Highly saline pore fluids in the rock matrix of a granitic batholith on the Canadian Shield. Proceedings of the 30th Int. Geological Congress, Beijing, China.

Gascoyne, M., Scheier, N.W. and Stevenson, D.R. (1999) Application of Hydrogeochemical Data to Groundwater Flow and Radionuclide Transport modelling in the Canadian Nuclear Fuel Waste Management Program. In Proceedings of Workshop on Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Borgholm, Sweden, September 1997, pp117-134. Nuclear Energy Agency of the OECD, Paris, France.

Geier, J., Tirén, S., Dverstorp, B. and Glynn, P. (1996) SITE-94. Site-Specific Base Data for the Performance Assessment. SKI Report 96:10. SKI Stockholm.

Glynn, P.D. and Voss, C.I. (1999) Geochemical Characterisation of Simpevarp Ground Waters near the Äspö Hard Rock Laboratory, SKI Report 96:29. SKI Stockholm.

Glynn, P.D., Voss, C.I. and Provost, A.M. (1999) Deep penetration of oxygenated meltwaters from Warm Based ice-Sheets into the Fennoscandian Shield Use of Hydrogeochemical Information. In: Proceedings of Workshop on Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Borgholm, Sweden, September 1997, pp201-241. Nuclear Energy Agency of the OECD, Paris, France.

Grenthe, I., Stumm, W., Laaksuharju, J., Nilsson, A.-C. and Wikberg, P. (1992) Redox potentials and redox reactions in deep groundwater systems. Chemical Geology, 98, 131-150

Gurban, I., Laaksoharju, J., Made, B. and Ledoux, E. (1999) Uranium transport around the reactor zone at Okelobondo (Oklo): Data evaluation with M3 and HYTEC. Technical Report TR-99-36. SKB Stockholm.

Kamineni, D.C., Gascoyne, M., Melnyk, T.W., Frape, S.K. and Blomqvist, R. (1992) Cl and Br in mafic and ultramafic rocks: Significance for the origin of salinity in groundwater. In WRI-7, Proc. 7th Intl. Symposium on Water-Rock Interaction, Park City, USA, July 1992. (Y. Kharaka & A. Maest, eds), pp206-210. Balkema, Rotterdam.

Karlsson, F., Allard, B., Hummel, W., Sargent, F.P., Vieno, T., Voinis, S. Merceron, T. and Yoshikawa, H. (1995) Natural organic substances in granitic groundwater and their implications for nuclear waste disposal. In: Binding Models Concerning Natural Organic Substances in Performance Assessment. OECD-NEA Workshop, Baden, Switzerland (September 1995), pp45-54. Nuclear Energy Agency of the OECD, Paris, France.

Karnland, O. (1997) Bentonite swelling pressure in strong NaCl solution: Correlation between model calculations and experimentally determined data. Technical Report TR-97-31. SKB Stockholm.

Karnland, O., Sandén, T., Johannesson, L-E., Eriksen, T.E., Jansson, M., Wold, S., Pedersen, K. Motamedi, M and Rosborg, B. (2000) Long term test of buffer material: Final report on the pilot parcels. Technical Report TR-00-22. SKB Stockholm.

King, F., Ahonen, L., Taxén, C., Vuorinen, U. and Werme, L. (2001) Copper corrosion under expected conditions in a deep geologic repository. Technical Report TR-01-23. SKB Stockholm.

Laaksoharju, M. (1999) Groundwater characterisation and modelling: problems, facts and possibilities. Technical Report TR-99-42. SKB Stockholm.

Laaksoharju, M., Smellie, J., Ruotsalainen, P. and Snellman, M. (1993) An approach to quality classification of deep groundwaters in Sweden and Finland. Technical Report TR-93-27. SKB Stockholm.

Laaksoharju, M., Smellie, J. Nilsson, A-C. and Skårman, C. (1995a) Groundwater sampling and chemical characterisation of the Laxemar deep borehole KLX02. Technical Report TR-95-05. SKB Stockholm.

Laaksoharju, M., Degueldre, C. and Skårman, C. (1995b) Studies of colloids and their importance for repository performance assessment. Technical Report TR-95-24. SKB Stockholm.

Laaksoharju, M., Gurban, I. and Skårman, C. (1998) Summary hydrochemical conditions at Aberg, Beberg and Ceberg. Technical Report TR-98-03. SKB Stockholm.

Laaksoharju, J., Tullborg, E.-L, Wikberg, P., Wallin, B. and Smellie, J. (1999a) Hydrogeochemical conditions and evolution at the Äspö HRL, Sweden. Applied Geochemistry, 14, 835-839

Laaksoharju, M., Skårman, C. and Skårman E. (1999b) Multivariate mixing and mass balance (M3) calculations, a new tool for decoding hydrogeochemical information. Applied Geochemistry, 14, 861-871

Laaksoharju, M., Andersson, C., Gurban, I. and Gascoyne, M. (2000) Demonstration of M3 modelling of the Canadian Whiteshell research area (WRA) hydrogeochemical data: OPG/SKB M3 modelling project. Technical Report TR-01-37. SKB Stockholm.

Landström, O. and Tullborg, E.L. (1995) Interactions of trace elements with fracture filling minerals from the Äspö Hard Rock Laboratory. Technical Report TR-95-13. SKB Stockholm.

Langmuir, D. (1997) Aqueous Environmental Geochemistry. Prentice-Hall Inc.

Louvat, D., Ledoux, E. and Winberg, A. (1999) Oklo natural analogue: Hydrochemical constraints on the radionuclide transport modelling at Bagombé. In: Proceedings of Workshop on Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Borgholm, Sweden, September 1997, pp169-174. Nuclear Energy Agency of the OECD, Paris, France.

Macalady, D.L., Langmuir, D., Grundl, T. and Elzerman, A. (1990) Use of model-generated Fe^{3+} ion activities to compute Eh and ferric oxyhydroxides solubilities in anaerobic systems. In: Chemical Modeling in Aqueous Systems II, ed. D.C. Melchior and R L Bassett. Amer. Chem. Soc. Symp. Ser. 416, pp350-367. American Chemical Society, Washington, DC.

Mazurek, M. Smith, P.A. and Gautschi, A. (1992) Application of a realistic geological database to safety assessment calculations: An exercise in interdisciplinary communication. In WRI-7, Proc. 7th Intl. Symposium on Water-Rock Interaction, Park City, USA, July 1992. (Y. Kharaka & A. Maest, eds) pp407-411. Balkema, Rotterdam.

Metcalfe, R., Milodowski, A.E. and Noy, D.J. (1999) Hydrogeochemical Evidence Supporting Models for Groundwater Flow around Sellafield, UK. In: Proceedings of Workshop on Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Borgholm, Sweden, September 1997, pp315-328. Nuclear Energy Agency of the OECD, Paris, France.

Miller, W., Alexander, R., Chapman, N., McKinley, and Smellie, J. (1994) Natural Analogue Studies in the Geological Disposal of Radioactive Wastes. Nagra Technical Report 93-03

Milton, G.M. (1987) Palaeohydrological inferences from fracture calcite analyses: an example from the Stripa Project, Sweden. In: Proceedings of the Conference on Isotope Geochemistry of Groundwater and Fracture Material in Plutonic Rock, Quebec, Canada, October 1986. Applied Geochemistry, 2, 33-36

Moser, H., Wolf, M. Fritz, P., Fontes, J-Ch., Florkowski, T. and Payne, B.R. (1989) Deuterium, oxygen-18, and tritium in Stripa groundwater. Geochimica et Cosmochimica Acta, 53, 1757-1763.

Nirex (1996) Rock Characterisation Facility, Longlands Farm, West Cumbria: Report on Baseline Groundwater Pressures and Hydrochemistry. Sellafield Geological and Hydrogeological Investigations. Nirex Science Report No SA/96/006. UK Nirex Ltd, Harwell.

Nirex (1997a) Hydrochemistry of Sellafield: 1997 Update. Sellafield Geological and Hydrogeological Investigations. Nirex Science Report No SA/97/089. UK Nirex Ltd, Harwell.

Nirex (1997b). Evaluation and Interpretation of Carbon Isotope and Tritium Data for Groundwater Samples from Deep Boreholes at Sellafield. Nirex Science Report No. SA/97/094. UK Nirex Ltd, Harwell.

Nirex (1998) Sellafield Geological and Hydrogeological Investigations. Compilation of Reconnaissance Studies for Selected Isotope, Gas and Trace Element Data from Sellafield. Sellafield Geological and Hydrogeological Investigations Nirex Science Report No SA/97/090. UK Nirex Ltd, Harwell.

Nordstrom, D.K. and Puigdomenech, I. (1986) Redox chemistry of deep groundwaters in Sweden. Technical Report TR-86-03. SKB Stockholm.

Nordstrom, D.K., Ball, J.W., Donahoe, R.J. and Whittemore, D. (1989) Groundwater chemistry and water-rock interactions at Stripa. Geochimica et Cosmochimica Acta, 53, 1727-1740.

Ohlsson, Y. and Neretnieks, I. (1995) Literature survey of matrix diffusion theory and of experiments and data including natural analogues. Technical Report TR-95-12. SKB Stockholm.

Paces, J.B., Peterman, Z.E., Neymark, L.A., Whelan, J.F. and Marshall, B.D. (1999) Constraints on Quaternary Unsaturated- and Saturated-Zone Hydrology from Geochronological and Isotopic Studies of Calcite and Silica, Yucca Mountain, Nevada, USA In: Proceedings of Workshop on Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Borgholm, Sweden, September 1997, pp329-336. Nuclear Energy Agency of the OECD, Paris, France.

Parkhurst, D.L. (1995) User's Guide to PHREEQC – a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. US Geological Survey Water-Resources Investigations Report 95-4227.

Pitkänen, P., Löfman, J., Korkaelaakso, J., Koskinen, L., Ruotsalainen, P., Hautojärvi, A. and Äikäs, T. (1999) Integration and consistency Testing of Groundwater Flow Models with Hydrogeochemistry in Site Investigations in Finland. In: Proceedings of Workshop on Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Borgholm, Sweden, September 1997, pp93-105. Nuclear Energy Agency of the OECD, Paris, France.

Puigdomenech, I., Ambrosi, J-P, Eisenlohr, Lartigue, J-E., Banwart, S.A., Bateman, K., Milodowski, A.E., West, J.M., Griffault, L., Gustafsson, E., Hama, K., Yoshida, H., Kotelnikova, S., Pedersen, K., Michaud, V., Trotignon, L, Rivas Perez, J. and Tullborg, E.-L (2001) O_2 depletion in granitic media: the REX project Technical Report TR-01-05. SKB Stockholm.

Puigdomenech, I. and Taxén, C. (2000) Thermodynamic data for copper Implications for the corrosion of copper under repository conditions. Technical Report TR-00-13. SKB Stockholm.

Savage, D. and Arthur, R.C. (1997) pH and pCO_2 in groundwaters in fractured hard rocks. Extended Abstracts for the Geofluids II Conference (J. Hendry, P. Carey, J. Parnell, A. Ruffell, and R. Worden, eds). pp 399-402.

Sheppard, M.I., Stephenson, M., Thomas, D.A., Reid, J.A.K., Thibault, D.H., Lacroix, M. and Ford, S. (1995) Aquatic-terrestrial partitioning of deep groundwater discharge using measured helium fluxes. Environmental Science and Technology, 29, 1713-1721.

SKB (1999). Deep repository for spent nuclear fuel SR97 - Post-closure safety. Main report, vol. 1. Technical Report TR-99-06, SKB, Stockholm.

SKB (2000a). Geoscientific programme for investigation and evaluation of sites for the deep repository. Technical Report TR-00-20. SKB Stockholm.

SKB (2000b). Integrated account of method, site selection and programme prior to the site investigation phase. Technical Report TR-01-03. SKB Stockholm.

SKB (2001a). Platsundersökningar: Undersökningsmetoder och generellt genom-förandeprogram. Report R-01-10. SKB Stockholm.

SKB (2001b). Site investigations, Investigation methods and general execution programme. Technical Report TR-01-29. SKB Stockholm.

SKI (2001). The Swedish Nuclear Power Inspectorate's Review Statement on the Swedish Nuclear Fuel and Waste Management Company's RD&D programme 98 Supplement. SKI Report 01:32. SKI, Stockholm.

Smellie, J. and Laaksoharju, M. (1992) The Äspö Hard Rock Laboratory: Final evaluation of the hydrogeochemical pre-investigations in relation to existing geologic and hydraulic conditions. Technical Report TR 92-31. SKB Stockholm.

Smellie, J.A.T., Bath, A.H. and Karlsson, F. (1999) Applications of Hydrogeochemistry in Performance Assessment. In: Proceedings of Workshop on Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Borgholm, Sweden, September 1997, pp 43-62. Nuclear Energy Agency of the OECD, Paris, France.

Stephenson, M., Schwartz, W.J., Evenden, L.D. and Bird, G.A. (1992) Identification of deep groundwater discharge areas in the Boggy Creek Catchment, southeastern Manitoba, using excess aqueous helium. Canadian Journal of Earth Science, 29, 2640-2652.

Thury, M. Gautschi, A., Mazurek, M., Müller, W.H., Naef, H., Pearson, F.J. Vomvoris, S. and Wilson, W. (1994) Geology and Hydrogeology of the Crystalline Basement of Northern Switzerland. Synthesis of Regional Investigations 1981-1993 within the Nagra Radioactive Waste Disposal Programme. Nagra Technical Report 93-01. Nagra, Wettingen.

Tullborg, E-L. (1997) Recognition of low-temperature processes in the Fennoscandian Shield. Unpublished PhD thesis, A17. Earth Sciences Centre, Department of Geology, Göteborg University, Sweden.

Tullborg, E-L. (1999) Assessment of Redox Conditions Based on Fracture Mineralogy. In: Proceedings of Workshop on Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Borgholm, Sweden, September 1997, pp341-353. Nuclear Energy Agency of the OECD, Paris, France.

Toulhoat, P., Beaucaire, C., Michard, G. and Ouzounian, G. (1992) Chemical Evolution of Deep Groundwaters in Granites, Information Acquired form Natural Systems. In: Proceedings of Workshop on Palaeohydrogeological Methods and their Applications, Paris, November 1992. pp105-116. Nuclear Energy Agency of the OECD, Paris, France.

Viani, B.E. and Bruton, C.J. (1997) In assessing the rôle of cation exchange in controlling groundwater chemistry during fluid mixing in fractured granite at Äspö, Sweden. In: Evolution of the groundwater chemistry at the Äspö Hard Rock Laboratory. Proceedings of the Second Äspö International Geochemistry Workshop, June 1995, (M. Laaksoharju and B. Wallin, eds). International Cooperation Report 97-04. SKB Stockholm.

Vieno, T. (2000) Groundwater salinity at Olkiluoto and its effects on a spent fuel repository. Posiva Report 2000-11. Posiva Oy, Helsinki.

Wersin, P., Spahiu, K. and Bruno, J. (1994) Kinetic modelling of bentonite-canister interaction – Long-term predictions of copper canister corrosion under oxic and anoxic conditions. Technical Report TR-94-25. SKB, Stockholm.

Wikberg, P., Axelsen, K. and Fredlund, F. (1987) Deep groundwater chemistry. Technical Report TR-87-07. SKB Stockholm.

Wikberg, P., Smellie, J., Wallin, B., Tullborg, E-L and Laaksoharju, M. (1992) Experiences from geohydrochemical investigations at the Äspö HRL site in Sweden. In: Proceedings of Workshop on Palaeohydrogeological Methods and their Applications, Paris, November 1992. pp 219-236. Nuclear Energy Agency of the OECD, Paris, France.

Wolery, T.J. et al. (1990) Current status of the EQ3/6 software package for geochemical modeling. In: Chemical Modeling in Aqueous Systems II (D C Melchior and R L Bassett, eds). ACS Symposium Series 416. American Chemical Society, Washington, D.C.